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VELOCITY AND MASS DISTRIBUTIONS RESULTING FROM THE LATERAL DIFFUSION OF A CURRENT IN A STRATIFIED MEDIUM ON A ROTATING EARTH.

BY

G. GRIMMINGER.

David W. Taylor Model Basin, Navy Dept., Washington, D. C.

PART II.

C. Lateral Diffusion of a Circular Vortex in a Medium Composed of a Single Layer.

In Part I we have considered only the case when the main motion was in the x-direction, that is, when the main motion was that of straight parallel flow. We shall now consider the diffusion process when the main motion is in concentric circles as in the circular vortex. Before considering the case of a stratified medium it will first be necessary to have the solution for the diffusion of a circular vortex in a single layer.

Using the following notation:

u = tangential component,
v = radial component, positive outward,
r = radius vector, positive outward,
H = elevation of free surface,

then from considerations of momentum, the equation of motion in the u direction is easily found to be

$$\frac{d}{dt}(r^2uH) = -fvr^2H + \frac{\partial}{\partial r}\left(\frac{\tau}{\rho}r^2H\right). \tag{47}$$

If we now assume as before that the motion is quasistatic, that is, that changes in the motion take place so slowly that approximate

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dynamic equilibrium exists, then the above equation reduces to

$$0 = -fvr^2H + \frac{\partial}{\partial r}\left(\frac{\tau}{\rho} r^2H\right). \tag{48}$$

Since the centrifugal force is quite small in extra-tropical current systems, it will be neglected in the equation of motion in the v direction which then becomes the (geostrophic) gradient wind relation

$$u = \frac{1}{\rho f}\frac{\partial p}{\partial r} = \frac{g}{f}\frac{\partial H}{\partial r}. \tag{49}$$

The equation of continuity is

$$\frac{\partial}{\partial t}(rH) + \frac{\partial}{\partial r}(vrH) = 0. \tag{50}$$

By taking the partial derivative of (48) with respect to r and combining with (50), v can be eliminated; and if the substitution $y = (r^2/2)$ is used, we then have

$$f\frac{\partial H}{\partial t} + \frac{\partial^2}{\partial y^2}\left[2y\frac{\tau}{\rho}H\right] = 0 \tag{51}$$

for the equation of motion of a fluid column of height H. Using $\tau/\rho = \nu(\partial u/\partial r - u/r)$ as the expression for the shearing stress and $\nu = (\nu_0 H_0/H)$, as before, for the eddy viscosity and by making use of the gradient wind relation, (51) becomes

$$\frac{\partial H}{\partial t} + \frac{g}{f^2}\nu_0 H_0 \frac{\partial^2}{\partial y^2}\left[(2y)^2\frac{\partial^2 H}{\partial y^2}\right] = 0,$$

where H_0 is used to represent the height of the homogeneous atmosphere. This equation is further simplified by the substitution

$$\eta = \frac{2y}{\lambda^2} = \frac{r^2}{\lambda^2}, \quad \text{and} \quad s = \frac{16\nu_0 t}{\lambda^2},$$

giving

$$\frac{\partial H}{\partial s} + \frac{\partial^2}{\partial \eta^2}\left[\eta^2\frac{\partial^2 H}{\partial \eta^2}\right] = 0 \tag{52}$$

as the final form of the equation of motion.

The solution of this equation as derived in Appendix 4 is

$$\Delta H(\zeta, s) = H - H_0 = \int_0^\infty \epsilon^{-\frac{\sigma^4 s}{16}} J_0(\sigma\zeta)\sigma d\sigma \int_0^\infty \Delta H_i(\alpha) J_0(\sigma\alpha)\alpha d\alpha, \tag{56}$$

where $\zeta = \sqrt{\eta} = (r/\lambda)$, $2\gamma = \sigma$, and α represents the same quantity as ζ.

The choice of ΔH_i, the initial distribution of ΔH, is now at our disposal, and it is convenient to do this in such a way, if possible,

that the last integral on the right can be evaluated. For this reason we have chosen

$$\Delta H_i = H_i - H_0 = -\Delta\epsilon^{-\beta^2\alpha^2},$$

which also seems a reasonable assumption from physical considerations. The initial elevation profile thus approaches the height H_0 of the homogeneous atmosphere at infinity and dips down from this value at the center of the vortex by an amount Δ. Since

$$\int_0^\infty \epsilon^{-\beta^2\alpha^2} J_0(\sigma\alpha)\alpha d\alpha = \frac{1}{2\beta^2}\epsilon^{-\frac{\sigma^2}{4\beta^2}},^4$$

we have

$$\frac{\Delta H}{\Delta} = \frac{-1}{2\beta^2}\int_0^\infty \epsilon^{-\left(\frac{\sigma^4\zeta}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0(\sigma\zeta)\sigma d\sigma \tag{57}$$

for the elevation profile.

Using the gradient wind relation to obtain the velocity profiles, we find that

$$u = \frac{g}{f\lambda}\frac{\partial H}{\partial\zeta} = \frac{g}{f\lambda}\frac{\partial(\Delta H)}{\partial\zeta} = \frac{\Delta}{2\beta^2}\frac{g}{f\lambda}\int_0^\infty \epsilon^{\left(-\frac{\sigma^4\zeta}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0'(\sigma\zeta)\sigma^2 d\sigma$$

or

$$\frac{1}{\Delta}\sqrt{\frac{H_0}{g}}\,u = \frac{1}{2\beta^2}\int_0^\infty \epsilon^{\left(-\frac{\sigma^4\zeta}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_1(\sigma\zeta)\sigma^2 d\sigma. \tag{58}$$

The initial velocity distribution corresponding to the initial elevation profile for the free surface is easily found to be

$$\frac{1}{\Delta}\sqrt{\frac{H_0}{g}}\,u_i = 2\beta^2\alpha\epsilon^{-\beta^2\alpha^2}. \tag{59}$$

The profiles for the single layer have not been computed; we proceed instead to the more interesting case of a stratified medium composed of two homogeneous layers.

D. Lateral Diffusion of a Circular Vortex in a Stratified Medium Composed of Two Layers.

As in the case of rectilinear flow the stratified medium is taken to consist of two fluid layers, a lower one of density ρ_2 and a warmer one above of density ρ_1. The equations of motion are

$$\begin{cases} \dfrac{\partial K_1}{\partial s_1} + \dfrac{\partial^2}{\partial\eta^2}\left[\eta^2\dfrac{\partial^2 K_1}{\partial\eta^2}\right] = 0 & \text{for the upper layer, and} \\ \dfrac{\partial K_2}{\partial s_2} + \dfrac{\partial^2}{\partial\eta^2}\left[\eta^2\dfrac{\partial^2 K_2}{\partial\eta^2}\right] = 0 & \text{for the lower layer,} \end{cases} \tag{60}$$

[4] See Watson: "Bessel Functions," p. 393.

where

$$(61)\qquad \begin{cases} K_1 = D_1 + \sqrt{\dfrac{\rho_2}{\rho_1}}\, D_2, & K_2 = D_1 - \sqrt{\dfrac{\rho_2}{\rho_1}}\, D_2, \\ s_1 = s\left(1 + \sqrt{\dfrac{\rho_1}{\rho_2}}\right), & s_2 = s\left(1 - \sqrt{\dfrac{\rho_1}{\rho_2}}\right). \end{cases}$$

D_2 is the thickness of the lower layer and D_1 that of the upper layer.

For initial conditions we shall assume that we have a warm upper layer with a cyclonic wind distribution and a cold lower layer which is a rest (zero pressure gradients at the ground); this would correspond to an upper level cyclone overlying a cold air mass. It is also possible, no doubt, to prescribe an initial condition such that the lower layer will have anticyclonic rotation, and thus to study a system composed of an upper level cyclone overlying an anticyclone; this will not be attempted here. Since we shall use the same initial condition for the upper layer as that prescribed above for the circular vortex in a single layer, the elevation of the free surface H_i is given by

$$(62)\qquad H_i = D_{1i} + D_{2i} = H_\infty - \Delta_1 \epsilon^{-\beta^2\alpha^2},$$

where the subscript i refers to initial conditions, and H_∞ is the elevation of the free surface at infinity.

Since we shall impose the initial condition of zero pressure gradient at the ground, the thickness of the lower layer must be of the form $D_{2i} = \Delta_2 \epsilon^{-\beta^2\alpha^2}$. Hence

$$D_{1i} = H_\infty - \Delta_1 \epsilon^{-\beta^2\alpha^2} - D_{2i} = H_\infty - (\Delta_1 + \Delta_2)\epsilon^{-\beta^2\alpha^2}.$$

From the expression for D_{2i} it will be noted that although the cold layer does not intersect the ground at an angle, it nevertheless becomes increasingly close to it at distances far enough removed from the axis of the vortex. The initial elevation profiles for the free surface and internal boundary corresponding to the initial conditions assumed above are shown schematically in Fig. 13.

Using the above, one now finds that

$$K_{1i} = H_\infty + \left[\left(\sqrt{\frac{\rho_2}{\rho_1}} - 1\right)\Delta_2 - \Delta_1\right]\epsilon^{-\beta^2\alpha^2},$$

$$K_{2i} = H_\infty - \left[\left(\sqrt{\frac{\rho_2}{\rho_1}} + 1\right)\Delta_2 + \Delta_1\right]\epsilon^{-\beta^2\alpha^2}.$$

Since $K_{1i\infty} = H_\infty$, let

$$(62)\qquad \begin{cases} \Delta K_{1i} = K_{1i} - H_\infty = \Delta_1' \epsilon^{-\beta^2\alpha^2} \equiv \left[\left(\sqrt{\dfrac{\rho_2}{\rho_1}} - 1\right)\Delta_2 - \Delta_1\right]\epsilon^{-\beta^2\alpha^2}, \\ \Delta K_{2i} = K_{2i} - H_\infty = \Delta_2' \epsilon^{-\beta^2\alpha^2} = -\left[\left(\sqrt{\dfrac{\rho_2}{\rho_1}} + 1\right)\Delta_2 + \Delta_1\right]\epsilon^{-\beta^2\alpha^2}. \end{cases}$$

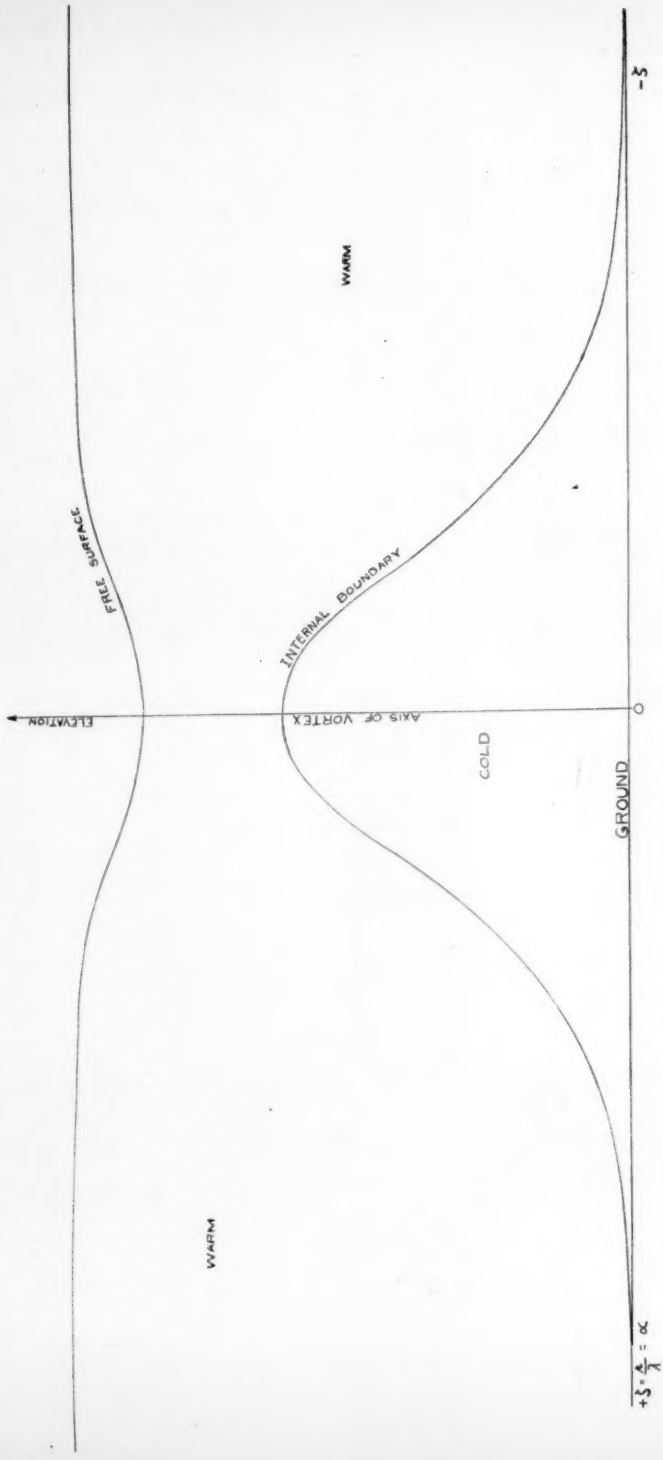

FIG. 13. Initial elevation profiles for the double layer circular vortex. Schematic.

Since ΔK_{1i} and ΔK_{2i} are of the same form as ΔH_i for the single layer vortex, we have that

$$(63)\quad \Delta K_1 = K_1 - H_\infty = \frac{\Delta_1'}{2\beta^2}\int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_1}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0(\sigma\zeta)\sigma d\sigma$$

$$\equiv \frac{\Delta_1'}{2\beta^2} Q(s_1, \zeta) \equiv \frac{\Delta_1'}{2\beta^2} Q_1 \quad \text{say,}$$

and

$$\Delta K_2 = K_2 - H_\infty = \frac{\Delta_2'}{2\beta^2}\int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_2}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0(\sigma\zeta)\sigma d\sigma$$

$$\equiv \frac{\Delta_2'}{2\beta^2} Q(s_2, \zeta) = \frac{\Delta_2'}{2\beta^2} Q_2,$$

where for brevity we have put

$$(65)\quad \int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_1}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0(\sigma\zeta)\sigma d\sigma = Q_1,$$

and

$$(66)\quad \int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_2}{16}+\frac{\sigma^2}{4\beta^2}\right)} J_0(\sigma\zeta)\sigma d\sigma = Q_2.$$

We thus find that

$$(67)\quad \begin{cases} K_1 = H_\infty + \dfrac{\Delta_1'}{2\beta^2} Q_1, \\ K_2 = H_\infty + \dfrac{\Delta_2'}{2\beta^2} Q_2. \end{cases}$$

From relations (61) it is easily found that

$$D_1 = \frac{K_1 + K_2}{2} = H_\infty + \frac{\Delta_1'}{4\beta^2} Q_1 + \frac{\Delta_2'}{4\beta^2} Q_2,$$

and

$$D_2 = \frac{1}{2}\sqrt{\frac{\rho_1}{\rho_2}}(K_1 - K_2) = \frac{1}{2}\sqrt{\frac{\rho_1}{\rho_2}}\frac{1}{2\beta^2}[\Delta_1' Q_1 - \Delta_2' Q_2].$$

From the assumed initial condition of zero pressure gradient at the ground it follows that

$$\rho_1 D_{1i0} + \rho_2 D_{2i0} = \rho_1 H_\infty,$$

or

$$\rho_1 H_\infty - \rho_1(\Delta_1 + \Delta_2) + \rho_2 \Delta_2 = \rho_1 H_\infty.$$

Hence,

$$\Delta_2 = \frac{\rho_1}{\rho_2 - \rho_1}\Delta_1$$

and

$$\Delta_1' = \left[\left(\sqrt{\frac{\rho_2}{\rho_1}} - 1\right)\frac{\rho_1}{\rho_2 - \rho_1} - 1\right]\Delta_1,$$

$$\Delta_2' = -\left[\left(\sqrt{\frac{\rho_2}{\rho_1}} + 1\right)\frac{\rho_1}{\rho_2 - \rho_1} + 1\right]\Delta_1.$$

It follows that

$$(68)\quad D_1 = H_\infty + \frac{1}{4\beta^2}\left\{\left[\left(\sqrt{\frac{\rho_2}{\rho_1}} - 1\right)\frac{\rho_1}{\rho_2 - \rho_1} - 1\right]Q_1 - \left[\left(\sqrt{\frac{\rho_2}{\rho_1}} + 1\right)\frac{\rho_1}{\rho_2 - \rho_1} + 1\right]Q_2\right\}\Delta_1,$$

$$(69)\quad D_2 = \frac{1}{4\beta^2}\sqrt{\frac{\rho_1}{\rho_2}}\left\{\left[\left(\sqrt{\frac{\rho_2}{\rho_1}} - 1\right)\frac{\rho_1}{\rho_2 - \rho_1} - 1\right]Q_1 + \left[\left(\sqrt{\frac{\rho_2}{\rho_1}} + 1\right)\frac{\rho_1}{\rho_2 - \rho_1} + 1\right]Q_2\right\}\Delta_1.$$

If p_0 denote the pressure at the ground, then

$$p_0 = \rho_1 g D_1 + \rho_2 g D_2,$$

and if we let $p_{0\infty} = \rho_1 g H_\infty$, the constant pressure at the ground at infinity, we then find by combining (68) and (69) that

$$(70)\quad \frac{p_0 - p_{0\infty}}{\rho_1 g \Delta_1} = \frac{1}{4\beta^2}\sqrt{\frac{\rho_2}{\rho_1}}\,(Q_2 - Q_1).$$

This is the expression for the pressure profile at the ground expressed as a difference from the constant pressure at the ground at distances far removed from the center of the vortex, and in units of $\rho_1 g \Delta_1$, the initial drop in pressure at the center of the vortex in the upper layer.

In the evaluation of (70) a temperature of 0° C. was assumed for the lower layer and 10° C. for the upper, so that $\rho_2/\rho_1 = 1.0367$, the same as for the cases of rectilinear flow.

The initial horizontal extent of the vortex depends upon the parameter β which is completely at our disposal. This has been assigned a value of 4 which means that the initial velocity distribution in the upper layer is such that the maximum velocity occurs at about 500 km. from the center of the vortex and the velocity drops to one tenth of its maximum value at about 1,000 km. The vortex can thus be considered as having initially a radius of 1,000 km. The initial velocity profile in the upper layer, as computed from equation (59), is shown in Fig. 14.

Owing to the complexity of the computations, the elevation and velocity profiles have not been worked out for the case of circular flow.

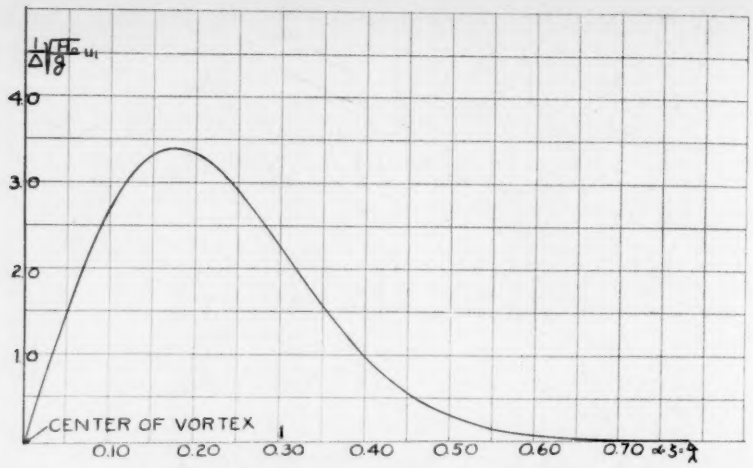

FIG. 14. Initial velocity distribution in upper layer of double layer circular vortex.

It is considered that the pressure profiles at the ground are probably the most interesting and illuminating result and these are the only profiles which have been computed for this case. The infinite integrals (65) and (66) defining Q_1 and Q_2 have been evaluated numerically and the resulting pressure profiles at the ground for two values of the time parameter s are shown in Fig. 15.

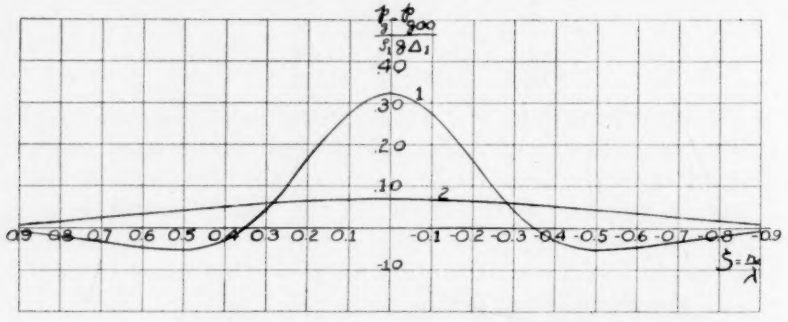

FIG. 15. Pressure profile at the ground; circular vortex, double layer.

Curve 1: $\frac{s}{16} = 0.141 \times 10^{-2}$.

Curve 2: $\frac{s}{16} = 0.360$.

The pressure changes at the ground at the center of the vortex are easily obtained from (70) by putting $\zeta = 0$, giving

$$\frac{p_{g0} - p_{g\infty}}{\rho_1 g \Delta_1} = \frac{1}{4\beta^2}\sqrt{\frac{\rho_2}{\rho_1}}\,(Q_{20} - Q_{10}), \tag{71}$$

where

$$Q_{10} = \int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_1}{16} + \frac{\sigma^2}{4\beta^2}\right)} \sigma d\sigma,$$

and

$$Q_{20} = \int_0^\infty \epsilon^{-\left(\frac{\sigma^4 s_2}{16} + \frac{\sigma^2}{4\beta^2}\right)} \sigma d\sigma.$$

The pressures at the ground at the center of the vortex computed from equation 71 for a few selected values of the time parameter s are given in Table 3.

TABLE 3.

Change of Pressure with Time at the Ground at the Center of the Double Layer Circular Vortex.

Time $\frac{s}{16}$	Pressure at Center of Vortex $\frac{p_{g0} - p_{g\infty}}{\rho g \Delta_1}$
.00001	.058
.0001	.206
.00141	.325
.001	.323
.01	.256
.1	.121
.360	.071
1.0	.044

This has been plotted on a logarithmic scale and the resulting curve is shown in Fig. 16.

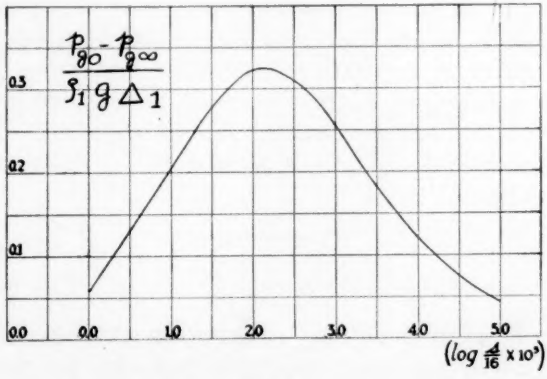

FIG. 16. Variation of pressure with time at the ground at the center of the double layer circular vortex.

From Fig. 15 it is seen that the immediate effect of the mixing process is to produce anticylogensis at the ground in a region central with the axis of the vortex and a trough or low pressure formation outside this central region. In the later stages the high pressure formation diminishes in intensity and at the same time is spread over a continually increasing area. The time rate of the pressure change at

the ground at the axis of the vortex is well brought out in Fig. 16, where it is seen that the maximum pressure rise amounts to about 33 per cent of $\rho_1 g\Delta_1$, the initial pressure drop in the upper layer. Assuming this latter to be, for example, 1 inch, this gives a maximum pressure rise at the ground of 0.33 inch. Or, considering also the trough formation corresponding to profile 1 of Fig. 15, this gives a total increase of pressure from trough to high pressure center of about 0.58 $\rho_1 g\Delta_1$ or 0.58 inch, which is not an uncommon value for anticyclogensis as found on the synoptic charts. The processes described here may thus be important factors not only for anticyclogensis in migratory anticyclones and the semi-permanent high pressure cells but also for the filling up of low pressure systems; i.e., the final stages of the occluded cyclone.

It should be pointed out that the character and intensity of the pressure changes at the ground resulting from lateral diffusion will depend upon the assumptions made concerning the initial distribution of pressure (i.e., velocity) in the upper layer. Thus, by using suitable initial conditions, it would no doubt be possible to use the above methods to show low pressure formation (deepening) at the ground as the result of the diffusion of an upper level (occluded) cyclone. There is hardly enough upper air wind data available to enable one to form any adequate idea as to the nature of the horizontal velocity distributions occurring with upper level cyclones so that the distribution used above must be considered as more or less theoretical in nature.

In conclusion, it may be said that the most important result of the investigation is to show how the lateral diffusion of currents in the upper atmosphere can produce significant pressure changes at the ground (cyclogensis and anticyclogensis) and, most important of all, that these pressure changes are dynamic in origin.

The author is indebted to Professor C. G. Rossby for suggesting this investigation.

APPENDIX 4.

SOLUTION OF THE EQUATION $\frac{\partial H}{\partial s} + \frac{\partial^2}{\partial \eta^2}\left[\eta^2 \frac{\partial^2 H}{\partial \eta^2}\right] = 0$ (52).

Assuming a solution of (52) in the form $H = S(s)N(\eta)$ it is found that the variables are separable and that one particular solution is $S = A\epsilon^{-\gamma^4 s}$ while the other is a solution of the ordinary differential equation

$$[\eta^2 N'']'' = \gamma^4 N, \tag{52a}$$

where the prime denotes differentiation with respect to η. The solution of this equation is $N = J_0(2\gamma\sqrt{\eta})$, so that a particular solution of (52) is $H = A\epsilon^{-\gamma^4 s} J_0(2\gamma\sqrt{\eta})$, where J_0 denotes the Bessel Function of zero order.

That $J_0(2\gamma\sqrt{\eta})$ is a solution of the ordinary differential equation (52a) can be shown as follows. Bessel's differential equation of the first order is

$$x^2\frac{dy^2}{dx^2} + x\frac{dy}{dx} + x^2y = 0, \tag{52b}$$

with the solution $y = J_0(x)$. Let $x = k\sqrt{\eta}$, $y = N$. Then

$$\frac{dy}{dx} = \frac{2\sqrt{\eta}}{k}N', \qquad \frac{d^2y}{dx^2} = \frac{4\eta}{k^2}N'' + \frac{2}{k^2}N',$$

where the prime denotes differentiation with respect to η. With these substitutions equation (52b) becomes

$$\eta^2N'' + \eta N' + \frac{k^2}{4}\eta N = 0$$

or

$$(\eta^2N'') = -\eta N' - \frac{k^2}{4}\eta N, \tag{52c}$$

which can also be written as

$$(\eta N')' = -\frac{k^2}{4}N. \tag{52d}$$

Differentiation of (52c) by η gives

$$(\eta^2N'')' = -(\eta N')' - \frac{k^2}{4}\eta N' - \frac{k^2}{4}N = -\frac{k^2}{4}\eta N'$$

by virtue of (52d). Differentiating again we have

$$(\eta^2N'')'' = -\frac{k^2}{4}(\eta N')' = \frac{k^4}{16}N \tag{52e}$$

by virtue of (52d). If we now let $k^4/16 = \gamma^4$, $k = 2\gamma$, equation (52e) becomes

$$(\eta^2N'')'' = \gamma^4N, \tag{52f}$$

which is identical with equation (52a). From (52b) the solution of (52f) is known to be

$$N = J_0(k\sqrt{\eta}) = J_0(2\gamma\sqrt{\eta})$$

and this must therefore be a solution of (52a).

Since equation (52) is linear, the solution may be written

$$H(\eta, s) = \int_0^\infty A(\gamma)\epsilon^{-\gamma^4s}J_0(2\gamma\sqrt{\eta})d\gamma.$$

Letting $2\gamma = \sigma$ and $\sqrt{\eta} = (r/\lambda) = \zeta$, the solution becomes

$$H = \frac{1}{2}\int_0^\infty A\left(\frac{\sigma}{2}\right)\epsilon^{-\frac{\sigma^4 s}{16}} J_0(\sigma\zeta)d\sigma. \tag{53}$$

From the Fourier Bessel Integral theorem, H_i, the initial distribution of H can be written in the form

$$H_i(\zeta) = \int_0^\infty J_0(\sigma\zeta)\sigma d\sigma \int_0^\infty H_i(\alpha)J_0(\sigma\alpha)\alpha d\alpha, \tag{54}$$

where α represents the same quantity as ζ. Hence

$$\frac{1}{2}A\left(\frac{\sigma}{2}\right) = \sigma\int_0^\infty H_i(\alpha)J_0(\sigma\alpha)\alpha d\sigma$$

and the solution is

$$H(\zeta, s) = \int_0^\infty H_i(\alpha)\alpha d\alpha \int_0^\infty \epsilon^{-\frac{\sigma^4 s}{16}} J_0(\sigma\zeta)\sigma d\sigma,$$

or, since the order of integration may be changed,

$$H(\zeta, s) = \int_0^\infty \epsilon^{-\frac{\sigma^4 s}{16}} J_0(\sigma\zeta)\sigma d\sigma \int_0^\infty H_i(\alpha)J_0(\sigma\alpha)\alpha d\alpha. \tag{55}$$

If we now let $\Delta H = H - H_0$, then since ΔH also satisfies (52), we can write

$$\Delta H(\zeta, s) = H - H_0 = \int_0^\infty \epsilon^{-\frac{\sigma^4 s}{16}} J_0(\sigma\zeta)\sigma d\sigma \int_0^\infty \Delta H_i(\alpha)J_0(\sigma\alpha)\alpha d\alpha, \tag{56}$$

which is the desired solution of equation (52).

COSMIC RAYS *

BY

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While I do not wish to alarm you unduly in these troublous times, a respect for the truth compels me to tell you that each one of you is at the present moment being shot about ten times per second by bullets whose speeds are a million times greater than the speed of a bullet from the highest power rifle known. Now I hasten to say that I am not the gangster who is responsible for this barrage of ammunition. The terrible fusilade is something which is going on all the time. There is nothing you can do about it; even an armor of lead will only enhance your troubles by irritating these bullets to the point of propagating their species in the armor and shooting you more frequently than if you had not sought to protect yourself. These mysterious bullets are the cosmic rays.

With morbid satisfaction I point out to you that each one of these bullets breaks up or damages about a million molecules in its journey through the body, so that each one of you has about ten million molecules damaged every second. Now I beg of you not to worry too much. Let me reassure you. I have on my coat a speck of dust. You cannot see it because it is too small. However, it contains a million times as many molecules as there are people on the earth. I think you will not miss a few million molecules.

Now how did we come to learn of the existence of these mysterious rays, and what are they? They first impressed their presence upon us in virtue of the power which they possess to make a gas like the atmosphere conduct electricity. We know that to conduct electricity a gas must be subjected continually to some kind of bombardment which breaks up its atoms; for it is through the existence of broken atoms that the electricity is conducted. The atoms, when broken, heal very quickly if left to themselves, so that to maintain the power to conduct electricity we must suppose the bombardment to be going on continually, in order that a sufficient number of sickly atoms necessary to provide the conducting power of the air may always be found.

Now the important thing which was discovered by Professor Victor F. Hess about 1911 was that the rate of destruction of atoms of gas in a

* Presented at the Stated Meeting held Wednesday, March 17, 1943. The lecture was given in lieu of the Director's Report for the year since the laboratory has been engaged exclusively upon secret government work during this period.

closed vessel increased very considerably with altitude, indicating that the bombardment increases as we ascend, a result to be expected if the bombarding bullets come from outside of our atmosphere and are absorbed to greater and greater extent as they penetrate, as bullets shot into a forest would be absorbed by the trees. By finding how the intensity of bombardment diminished as we descended into the atmosphere from above, it was possible to come to some conclusion as to the penetrating power of these rays—these cosmic bullets. At the time of their discovery, they were deemed to have a penetrating power ten times as great as that of any other kind of ray which we had previously met in the laboratory. We now know that their penetrating power is even greater than was then supposed, and that the measurable number of these rays can pass through as much as 75 feet of lead.

Since the work of Hess was done, many have followed in the field. R. A. Millikan and his collaborators have made careful measurements over lakes, on mountains, and during sea voyages. J. C. Clay, in Holland, was responsible for demonstrating a remarkable variation of cosmic ray intensity with latitude, and the effect was pursued by A. H. Compton and his collaborators in a world-wide survey. I am happy to say that, in all of the developments which have taken place, the Bartol Research Foundation has played a prominent part. T. H. Johnson and J. C. Street observed an asymmetry of the radiation as regards the east and west directions, an effect which was soon to be confirmed by further experiments of T. H. Johnson, and by A. H. Compton and L. W. Alvarez working simultaneously. These effects, taken in conjunction with the latitude variation, have played a profound part in establishing the nature of the cosmic rays. The Bartol Foundation placed apparatus on the two balloons which were sent high into the stratosphere by the National Geographic Society in collaboration with the U. S. Army Air Corps, and it also supplied the cosmic ray apparatus for the flight made by Professor and Mrs. Jean Piccard. In one of these flights the apparatus ascended to 72,000 feet, and our apparatus showed that the radiation continued to increase with altitude until at about 57,000 feet it started to diminish with further increase, a result observed also, and at about the same time, by E. Regener who, working in Germany, sent small pilot balloons with self-recording apparatus high into the atmosphere. Millikan and his collaborators have used similar self-recording apparatus in observations made in various parts of the world, and T. H. Johnson, and also S. A. Korff, both of our laboratory, have done important work with such balloons, using the radio technique for receiving records from the balloons, a method first developed in its important essentials by the meteorologists. S. A. Korff and E. T. Clarke have also been responsible for measurements made in the vicinity of the South Pole.

In previous reports, I have given accounts of the various contribu-

tions which the Foundation has made to our knowledge of the cosmic radiation. We have pursued it into deep mines, we have put it through many a third degree in our laboratory at Swarthmore. We have devised all sorts of Geiger counters to test its various activities. We have examined its behavior in strange devices called cloud chambers, which render the actual paths of the rays visible. We have examined in detail the interesting phenomena which it produces when it passes through matter of various kinds. Some of the rays live for only a short time, and we have measured how long they live.

As a result of such researches and similar researches performed by investigators in other laboratories, a great deal of information concerning this radiation has been accumulated, and it is to such information that we must look in order to find an answer to the question "What are the cosmic rays?"

The physicist in his studies has been led to a knowledge of the existence of certain things in the atomic world, and to some knowledge of the way in which these things act. Now physicists are very snooty people. It takes a very great deal of effort on the part of anything which is a candidate for the job of being a fundamental brick in nature's structure to gain an entrance to the community, and when the physicist encounters some new types of phenomena such as those met with in cosmic rays, he likes to avoid as far as possible the invocation of some entirely new agencies to explain the phenomena.

And so, like an honest conjurer, and a true physicist, I will open up my bag and show you what I have in it. I must show you what sorts of tricks and toys the man of science has accumulated which serve as bricks to imitate the structures and performances which he finds in nature, as the child imitates the castles and houses of his picture books with his wooden blocks.

Until nearly the end of the last century, it was believed that, in getting down to the atoms of the elements, we had reached the ultimate goal of divisibility of matter beyond which it was not possible to go. And then J. J. Thomson discovered a particle now called the negative electron, two thousand times lighter than the atom of hydrogen which, up to that time, had been considered to be the lightest thing in the universe. A remarkable thing about this particle was the fact that it appeared capable of being obtained from all substances, so that it was natural to regard it as one of the fundamental bricks, as one of the fundamental standardized parts of nature's structure.

Soon after the discovery of this particle, another of these fundamental bricks, the proton, made its appearance. It is a positively charged particle with a mass 2,000 times that of the electron; and in terms of the school of thought of the day, a thing so small that if everything in the universe were magnified until the proton attained the size of a pin's head, that pin's head would, on the same scale of magnifica-

tion, attain a diameter equal to the diameter of the earth's orbit around the sun.

For several years the hope of men of science was to explain all of the activities of the atoms and so all of the activities of nature in terms of the doings of these two particles, the electron and the proton. However, trouble of an ever-increasing nature arose from discoveries concerning the behavior of light. Three hundred years ago Sir Isaac Newton suggested that light was caused by streams of particles of some kind shot out by the source of light. However, it was found that this idea would not fit the facts and it seemed to become necessary to suppose that light really consisted of waves in some all-pervading medium, unobservable to our senses, these waves traveling out from the source of light like ripples from a stone thrown into a pond. Different lengths of waves were associated with different colors. The longest of the optical waves were those which gave rise to the sensation of red, the shortest were those corresponding to violet, with waves for all colors of the rainbow between. Then this idea became extended to include waves longer than those which could affect our sight, but which could produce heating effects. Then we came to think of wireless waves as simply an extension of this spectrum, as it is called, in the direction of the longer wave lengths. Again, in the direction of waves which are shorter than the violet rays, we saw the possibilities of what are now called ultraviolet rays, which, as you know, have important therapeutic uses. X-rays came to be looked upon as simply a special type of invisible light of still shorter wave length; and some of the rays from radium—the so-called gamma rays—also came into this class with a still shorter wave length. Thus, starting with the wireless waves which may have lengths of a mile or more, we came to think of a whole succession of waves passing through heat, light, ultraviolet light, X-rays, and gamma rays, this succession being one of gradually decreasing wave length, until in the gamma rays we pictured waves so short that a thousand million of them would cover but a third of an inch.

Just when these various agencies, light, X-rays, gamma rays, and so on, were being comfortably cataloged by the physicist as waves, some new properties were discovered for them, properties which seemed to demand that they have the characteristics of particles. Thus, they have one set of properties which make them look like waves and another set which make them look like particles. The best impression I can give you of these illusive things in the few minutes at my disposal this evening is to ask you to think of them as ghosts. A bullet is a kind of thing which can only be at one place at once and which strikes where it is. The electrons and protons are like bullets. A ghost is a creepy kind of thing which you feel can be everywhere always, a thing which only strikes at one place at a time, but which can strike anywhere.

These ghosts of physics, these things which represent light, X-rays, and the like, are called photons.

After taking these ghosts—the photons—into partnership with the negative electron and the proton, many thought that the membership list in the atomic club was closed, and the hope was to explain all the architecture of nature in terms of the activities of these particles. Now, in the seclusion of their private offices, where their colleagues could not hear their thoughts and chide them for being too bold, many physicists had wondered why there was not a positive counterpart to the negative electron—a thing having the same mass but opposite charge. They had wondered whether there might not be a neutral particle, and doubtless they had wondered many other wicked things. They had been more or less ashamed to bring these unwelcome debutantes into the society of their older forerunners. However, those aging forerunners showed increasing evidence of lacking enough pep to run the universe, to take charge, in fact, of the ever-increasing multitude of experimental facts. They preferred to continue performing the dance in which they had gained their great reputations, and failed to cooperate readily in the harmonization of any new experimental phenomena which did not conform to the old dances. Only after witnessing the shows put on by the electron, the proton, and their companion ghosts, the photons, for such a long time that he was sick of it, did the physicist go out fishing in the atomic world and catch a new particle, a neutral particle, the neutron. This seemed to give courage to other candidates for entrance into the court of atomic physics. There came the positron, the positive counterpart of the negative electron, heralded beforehand by a list of his credentials as supplied by the mathematical physicists, who claimed to know what he would look like when he was found. They were aggravatingly right. Before very long there came, as a matter of fact through the study of cosmic rays themselves, still another particle which could have a charge of either sign and which possessed a mass 200 times that of an electron. This particle also was preceded to some extent by its credentials in the form of the theoretical predictions of a Japanese physicist, Yukawa. So recent is this particle that the powers that be are yet quarreling over its christening. By some it has been called a "heavy electron," by others a "Yukon," by others a "barytron," by others a "mesotron," and the latest name is a "meson."

Now most of these particles came out about the time of the New Deal, and it was found that when they started to operate, the bank accounts didn't balance in the matter of conservation of energy. There was, in certain processes, an apparent disappearance of energy which could not be accounted for in known ways, so there was invented another particle, a neutrino, to provide the thief who stole the energy. The neutrino's sole function seems to be to own energy, for nobody has ever found him doing anything else. He is the supreme representative of

the radical's idea of a capitalist; or if you prefer, he is a kind of atomic miser, who never does anything with the wealth which he acquires.

As I have said already, we should like to see these cosmic rays as representatives, if possible, of some of the particles which represent the stock-in-trade of physics. In his choice between these various particles, the physicist has to proceed by the biblical instruction: "By their fruits shall ye know them." In arguing the possibilities, he is as one who, standing by a great jagged hole in a wall, hears the remark "Somebody fired a bullet through the wall." "No," he must remark, "such a large jagged hole could not have been caused by a bullet. That hole must have been caused by a large, slowly moving thing. An elephant is the kind of thing which would have made a hole like that." Or our physicist is in the position of one who, standing by a window pane with a clean-cut hole right through it, hears somebody remark: "A careless fellow poked his walking-stick through the window." "No," he must exclaim, "a walking-stick would have shattered the glass completely. Such a clean-cut hole must have been caused by a small thing of high velocity, like a bullet." And so it is by the characteristics of the cosmic rays that we must seek to decide what they are. However, even in this matter the procedure is not as simple as might at first sight be supposed. The physicist, in the light of the new phenomena presented to him, would like to have thought of the rays as electrons, or protons, or photons, one of those fundamental bricks of Nature's structure, in fact, which he had already admitted into the little atomic family at the time when cosmic ray phenomena were first observed. If, however, in those early days he had desired to think of the rays as electrons, he was faced with the difficulty that the highest energies with which he had been able to endow electrons in the laboratory were such as to permit them to go only through a fraction of an inch of lead. Since some of the cosmic rays were subsequently found to pass through 75 feet of lead, it was necessary for him to suppose that these rays, if electrons, had extraordinarily high energy. If he desired to think of the rays as photons, he was confronted with the fact that the photons of his laboratory experience would pass through only an inch or so of lead, so that to account for a passage through 75 feet of lead he had to suppose that the photons were of a very special kind. For a decision as to the *sense* in which they had to be of a special kind, he had to rely upon theories. His theories of earlier days told him that, in order to provide for great penetrating power, the photons should be of very short wave-length so as to possess very great energy. Thus, in judging between such things as charged particles and photons, the physicist had to extend his ideas far beyond his ordinary experience of such things, and that is what made the problem difficult. It is easy for you to form some concept of the difference between a conventional gangster and a conventional archbishop; but if I should increase the income of each of these individuals

to ten million dollars per year and endow them with all sorts of other opportunities, it would be a little difficult to predict beforehand in exactly what respects they would then differ. I do not wish to cast any doubts upon the fundamental morality of the archbishop or the fundamental wickedness of the gangster. I do say, however, that in these altered conditions the characteristics of both might be very different from what they are now.

In the light of our present knowledge of the behavior of things, the situation is then something like this: Electrons, in passing through matter, lose their energy in the first place by detaching other electrons from the outer structures of the atoms by which they pass. In virtue of their electric charge, their influence extends to some distance on all sides and they, as it were, tickle out participants of the dances going on in the various atoms which they approach in their journey. The amount of energy which they expend in each act is comparatively small compared with the energy which they possess. This characteristic of continually frittering away energy in small amounts is one which is common to all charged particles, and until comparatively recently it was believed, with a few exceptions, to be practically the only process by which charged particles lost their energy. These exceptions concerned the production of X-rays, and the like; but while important in themselves, they did not account for much of the energy lost by the charged particles. According to the beliefs current until comparatively recently, a photon, in passing through matter, did nothing at all except on rare occasions, until after what was, on the average, a very long journey, it experienced a direct impact with an atomic electron, to which it then communicated the whole, or a large part of its energy. Under such conditions, the electron then pursues its path as would any other electron, frittering away its energy by detaching other electrons from molecules.

Now within the last ten years we have come to realize that something else, very drastic and very important, can happen. The old theories taught us that the higher the energy of the photon the greater its power to penetrate matter, so that those who sought to explain the cosmic rays as photons had to suppose that the photons which could pass through 75 feet of lead were possessed of very great energy. However, both theory and the requirements of experiment began to urge upon us a new picture, a picture in which a photon of very high energy possessed the power to become what I may call "mathematically irritated" on approaching an atom and under these conditions, moreover, to change its state of existence, to disappear, in fact, and become replaced by a positive and negative electron which, before this event, did not exist at all. I am accustomed to cite the analogy of a spiritualistic séance in which the photon is the ghost, the positive and negative electrons represent the materialization of the ghost, and the atom is the medium.

Nothing happens to the medium except that it gets a fright; and even this fright is symbolized in the atomic problem by certain shiverings, or let us say oscillations, which the atom experiences during the materialization, but which subsequently subside, leaving it in its normal state.

Then again, the newer views tell us that in the case of electrons of very high energy, phenomena other than those associated with the slow frittering away of energy to which I have referred become important. One of these high energy electrons has a great chance of losing a large portion of its energy in the single act of the radiation of a photon as it passes by an atom. These photons, while of smaller energy than the electron, are still of high energy, however, and again possess the power to become irritated by the atoms which they approach, so that before long each of them materializes into a positive and a negative electron, which then repeat the story through several generations until the energy of the photons and electrons concerned have fallen so low that these more newly discovered phenomena are unimportant.

The neutral particle, the neutron, has characteristics quite different from those of the other particles. Being without electric charge, it does not produce the same kind of disruption of the outer structure of atoms and molecules as do charged particles. In fact, the neutron is the radical agitator of atomic physics. While a charged particle has, as it were, feelers extending out from itself in all directions in the shape of lines of electric force, feelers by which the atom becomes aware of its approach some time before it arrives, the uncharged neutron carries no such feelers. The atom does not know that it is there until it has already crept into the very nucleus itself, and then the trouble starts. The neutron says (mathematically, of course) "I need a place in the organization." The nucleus replies, again mathematically, "There is no place for you, everything is full up." "Then," says the neutron, "since I am here to stay, we must have a revolution, so that we can create a new atom in which I *can* be accommodated." As the result of all this, the atom blows up, shoots out some of its parts, the innocent bystanders, like bullets, in the form of radiations of different kinds, and finally settles down to become a new atom with the old neutron a now conservative member of the new organization. The process I have described in these somewhat facetious terms is the process by which a neutron, entering an atomic nucleus, causes it to become unstable, as the radium atom is naturally, and so to acquire the property of radioactivity, the property of spontaneous disintegration.

The mesotron is a charged particle, as I have said, about two hundred times heavier than the electron and ten times lighter than the proton. It was discovered independently by different methods by Carl Anderson of California, and by J. C. Street and E. C. Stevenson, both formerly of the Bartol Foundation. It is peculiar among all the particles in that it lives for only a short time. A very slowly moving

mesotron lives for only about two millionths of a second. However, the faster it moves, the longer it lives, and the more it gets done in its lifetime. Nature gave up this idea when she made man—or did she? Some of the most significant work in determining the age to which mesotrons live has been done at the Bartol Research Foundation.

The mesotron, being a charged particle, acts in this sense like any other charged particle in breaking up—ionizing, as we say—the molecules of air by which it goes. Unlike electrons, it does not go in for spiritualism. It does not emanate ghosts who subsequently produce more electrons which then produce more ghosts, and so ad infinitum. It goes on its way doing only one thing—ionizing the air—until it either dies in harness, or comes to the end of its tether by using up all its energy and then it waits around doing nothing until death overtakes it. When it dies, it gives birth to an electron, but a thief, in the shape of the neutrino, is also born and escapes with some of the family goods.

To return now to cosmic rays; when first their great penetrating power was realized, it was supposed that they must be of the nature of very hard X-rays, that is, of photon type, for at that time such things were the most penetrating things known and the theories of the day led us to believe that by assuming for the photons a sufficiently short wavelength we could make them as penetrating as we pleased. Charged particles were more or less ruled out for two reasons. In the first place, the energy which the particle would have to possess in order to provide for all the disruption of atoms it would have to bring about in passing through the atmosphere is such that more than a billion volts would be necessary to give it that energy. Such energies were regarded as fantastic twenty years ago, although today we do not shudder at energies ten million times as much. Then another objection came from the expected effect of the earth's magnetism.

The earth is a great magnet, and when a charged particle moves in the vicinity of a magnet its path is bent. The intensity of the earth's magnetic effect at any point is not great, but the extent of the influence is very wide, so that a charged particle coming towards the earth from outside can experience very great bending in its path in traveling distances comparable with the earth's radius. The bending is less, the greater the energy, and to illustrate the kind of magnitudes concerned, I may say that in the case of an electron approaching the earth in the magnetic equatorial plane, the electron would have to have an energy at least equal to that which would be given to it by twenty billion volts if it were to succeed in reaching the earth at all. If it had less than this, it would be turned back into space.

The drastic effect to be expected from the earth's magnetic field in the case of charged particles led formerly to the belief that if charged particles are responsible for cosmic rays, there should be large variations of cosmic ray intensity with latitude. At that time, no latitude varia-

tion was known, and this fact favored the photon hypothesis. Then, when a latitude effect was discovered, and when the variation in intensity with azimuth was discovered, these effects so characteristic of what was to be expected of charged particles brought the candidacy of these particles once more to the fore. The theory of the effect of the earth's magnetism was pursued more intensely and found to be capable of harmonizing everything in terms of a belief that the incoming radiation is composed of nothing but charged particles.

The kind of latitude effect found at sea-level was one according to which the cosmic ray intensity was a minimum at the magnetic equator and increased gradually as we went towards the poles, until a latitude of about 40° was reached, after which there was no further increase. This behavior was interpreted on the assumption that there was a distribution in energy among the incoming particles, and that at any latitude all particles below a certain limiting energy depending upon the latitude were cut out by the magnetic field. Theory showed that the minimum energy for entry was highest for the equator and decreased towards the poles. The increase of intensity on a journey from the equator towards the poles was attributed to the fact that more and more of the lower energy particles could get through the field as we proceeded on this journey. The cessation of the increase at 40° was explained by supposing that the minimum energy for entry at 40° was only just sufficient to enable rays with that energy to pass through the atmosphere so that, although the number of rays entering the atmosphere might be expected to continue to increase in the journey towards the poles, all of those rays over and above the rays entering at 40° would have such a low energy that they could not penetrate the atmosphere, and so would be unobserved at sea-level.

However, with all of this nicely settled, charged particles began to promote a difficulty from another angle, for it is obvious that since the rays of least energy entering at 40° could just pass through the atmosphere, all the rays entering at the equator should be able to pass through the atmosphere, and we should have no right to expect any increase of intensity with altitude at the equator. Such a result was, however, quite contrary to the facts. It was for this reason that I introduced the hypothesis that the rays, on passing through the atmosphere, shot out low energy secondary rays to an extent which increased with the energy of the primary rays themselves, so that high in the atmosphere, where the primary rays had not yet lost much energy by ionization, more secondary rays were shot out than at lower altitudes. This hypothesis provided for the necessary increase of the measured cosmic ray intensity with altitude at the equator. It was about this time that the quantum theory of atomic structure predicted this very kind of phenomenon for electrons and gave a more detailed story of its mechanism, the story which I have already sketched, in which the

photons—the ghosts—alternate with the material particles, the electrons, in producing successive generations of positive and negative electrons.

At this stage it was natural to play with the idea that the incoming radiation was composed of electrons. An incoming electron would, on encountering the atmosphere, soon give birth to a photon in the manner I have already cited. The photon, becoming mathematically irritated by its surroundings, soon decides to change its existence and, by itself dying, gives birth to a positive and negative electron. At first sight, one might suppose that through the creation of successive generations, the number of electrons would increase as we descended into the atmosphere. However, such an expectation is not justified because the progeny are continually losing energy by detaching electrons from molecules—by ionization, in fact—and the low energy progeny come to the end of their tether in this manner. At any point in the atmosphere we should expect, in fact, that there would be a birth rate and a death rate. At first, as we descend from above, the birth rate would be expected to be greater than the death rate, so that the number of electrons would increase as we descend. Finally, however, we should expect to reach a place where the birth rate and death rate were equal; and on further descent the death rate would exceed the birth rate, so that the number of rays would diminish with increasing depth in these regions.

Even if a photon were the primary entity entering the atmosphere, it would soon materialize into a positive and negative electron, and the story would proceed as before. We thus see how, through the agency of this multiplicative process, we should expect that, whether high energy photons or high energy electrons were the primary agencies which entered the atmosphere, we should find an increase of cosmic ray intensity as we descended into the atmosphere, followed by a decrease. The actual experimental realization of this phenomenon in the stratosphere flights, which showed a maximum in the cosmic ray intensity at an altitude of about 11 miles, provided strong confirmation of the theory of the multiplicative process as operative in the atmosphere. Nor have we since found occasion to discard the multiplicative idea, although we have found it necessary to modify our conceptions as to the actual primary particles which first enter the atmosphere, and for the following reasons:

It results from the rapidity of loss of energy by a primary high energy electron in passing through matter that, unless we are willing to admit energies which seem to be out of the realm of reason, nearly all of the primary electrons entering the atmosphere would be stopped before they had descended through more than a small fraction of the earth's atmosphere. The situation is as though in the higher regions of the atmosphere there were a department of immigration which stopped all the incoming immigrants and permitted only the children

born in the country and the subsequent generations to descend to the favored regions below.

Moreover, even the children are not allowed to go far, for when we make calculations in terms of the known atomic quantities associated with the rays, we find that it is unreasonable to expect that an appreciable fraction of the progeny of the primary parent could get down as far as the earth through our atmosphere. But we observe cosmic rays at the surface of the earth, and we observe them in coal mines and in other great depths, and in measurable amount down to distances of more than 250 meters under water. What is it that gets down to these great depths? Low energy electrons or photons could not travel as far as that because they have not enough energy, and high energy electrons or photons could not travel as far as that because they commit suicide too rapidly and give ultimately low energy progeny. The question thus arose—what other kinds of particles are there?

Whatever the nature of the particles primarily responsible for what is observed at sea-level, we must suppose that the representatives of these particles carry electric charges when they enter the atmosphere; for how else could we invoke the earth's magnetic field for the purpose of explaining the latitude and allied effects? It was suggested that the radiation observed at sea-level and below may consist of protons which there was reason to believe did not experience the multiplicative process characteristic of electrons. However, apart from all other difficulties, there is a fundamental difficulty in assuming protons to be operative appreciably at sea-level. For since the number of rays varies with altitude even in the vicinity of the earth's surface, we are in a position to measure just how many disappear in any assigned thickness. We can measure, for example, how many would end their existence in some measuring vessel in which we sought to measure the spurts of conducting power contributed to the gas as each ray passed through it. Now it is characteristic of protons, as of all charged particles, that they end their lives in a regular orgy of activity. Just before they die, they slay everything around them in the sense that they break up a much larger number of molecules per unit of their path than they do when they are far from the end of their lives. For an electron, the period of special activity just before death is so small that the remnants of the final party are hardly observable. However, the protons carry on in the hilarious mood for a time which is considerably longer, with the net result that the actual ending of the active life of a proton is something which would produce enough evidence to become measurable. We have investigated this matter at the Bartol Foundation, and the fact is that we do not find as much evidence of this kind as would be necessary to account for the number of rays which would be known to end their paths in our measuring apparatus, if we assumed these rays to be protons.

Until comparatively recently, it was very difficult to correlate the various known facts in these connections with the properties of any of the particles which atomic physics had placed at our disposal. Charged particles heavier than the proton would only have presented the difficulty in more acute form. The neutral particle, the neutron, was of no use in alleviating the difficulty, since it carried no electric charge and therefore could not make itself evident in the way that cosmic rays do. And then only a few years ago, it was found that the majority of cosmic rays observed at sea-level had, in actuality, a mass about 200 times that of the electron and one tenth that of the proton. These particles are the mesotrons of which I have already spoken. Our theories teach us that with a mass as *large* as this, the particle is relieved of the responsibilities of having to become the progenitor of a long line of offspring as does the high energy electron. However, with a mass as *small* as this—a mass ten times smaller than the mass of the proton, we are relieved of the embarrassment of having to predict that terrific increase of activity near the time of final retirement from active service which we were forced to predict in the case of the proton.

The mesotron loses energy only by ionization, and we can understand, therefore, how it can penetrate to the great depths at which we find the cosmic rays. The mesotron is the most penetrating thing in all physics.

> It flies through the air with the greatest of ease,
> But unlike the Man on the Flying Trapeze,
> It bumps against everything found on the way
> Till at last we have naught but a dead cosmic ray.

At this stage, therefore, and without further evidence, it was natural to assume that the mesotrons came to us from some source outside the atmosphere. Against this view, however, there arise three primary difficulties. The first arises from the fact that if we measure the energy of the mesotrons to be found, let us say, at sea-level and then extrapolate back to the top of the atmosphere, allowing for the loss of energy by ionization on the way, we find that in that place, before they had lost any of their energy by ionization, many of them had insufficient energy to have permitted them to get into the earth's atmosphere through the earth's magnetic field. It becomes necessary, therefore, to assume that some of the mesotrons at any rate are produced in the atmosphere itself and this, of course, incites us to assume that all of them are produced in the atmosphere if there should be any other circumstances which point to that conclusion.

A second piece of evidence favoring the view that the mesotrons are produced in our atmosphere arises from the fact which I have already cited to the effect that these mesotrons have only a limited life. They do not all live to the same age but, like men, have a certain

expectancy of life—a certain "mean life" as we call it—at birth. Moreover, the mean life is greater for those groups which are born with high energy than for those born at rest.

If the mesotron could live for ever, the theory of ionization, i.e. of the disruption of atoms by rays passing near or through them, leads us to expect that the fraction of the mesotrons which would be absorbed in a certain thickness of water would be the same as the fraction which would be absorbed in an equivalent thickness of air, equivalent, that is, in the sense that the masses per unit area are equal. This, at any rate, with slight modifications, concerning which the theoretical physicists are perfectly happy, represents the current view. If, however, the mesotron has a finite life, then the disappearance in the water will be less than in the very much longer thickness of air, since the time to penetrate the latter is so much greater than the time to penetrate the former. By comparing the absorption of mesotrons in air and water and seeing how much the ratio departs from what would be expected if the life of the mesotron were infinite, it has been possible to determine the average life of the mesotron, and it comes out to be of the order of two one-millionths of a second for mesotrons of small energy; and although the life increases with the energy, a factor of a million on the life would only give the mesotron two seconds to live. Such a situation is completely antagonistic, therefore, to the view that the mesotrons come from outside of our atmosphere, for even if they came from a body as near as the sun and traveled with the velocity of light, they would take eight minutes to get here and practically all would have died before they arrived.

But there is still further evidence in favor of the assumption that the mesotrons are produced within our atmosphere. I have already referred to the fact that the earth's magnetic field deviates the paths of charged particles to an extent depending upon their direction of approach, upon the latitude and, I may add, for any given direction, upon the sign of the charge, positive or negative. It is easier for positively charged particles to come in from the west than the east and the converse is true for negatively charged particles. Such observations as those of T. H. Johnson on the difference in intensity from the east and from the west, combined with observations of the variation with latitude, have led to the conclusion that practically all of the incoming radiation which is responsible for what we observe at sea-level is of the positive sign of charge. However, when we examine the *mesotrons* to be found at sea-level, we find from their deviations in magnetic fields that they are practically equally distributed as regards positive and negative sign of charge. This means that the mesotrons cannot themselves be the primary rays. They must have been brought into existence by some other primary which was itself positively charged, and which, therefore, entered the atmosphere in amounts varying with

latitude and direction to the extent determined by the fact that it was positively charged. We must then suppose that this primary ray coming into the atmosphere somehow or other creates mesotrons which continue its journey of flight, but which can very well have been created in equal numbers, positive and negative.

Although, as I have implied, it is very unlikely that an appreciable fraction of any electron rays entering our atmosphere, or of their progeny, could reach down to the earth, nevertheless, we do find electrons of considerable energy at sea-level, and Mr. W. E. Ramsey and I have found them in considerable amount even at great depths below sea-level. These electrons are produced by the mesotrons which, in addition to performing the relatively mild act of tickling electrons out of atoms in the process of ionization, occasionally hit them out with sufficient energy to cause them to function as measurable rays. Indeed, this act of the generation of high energy electrons by mesotrons has recently been observed. Moreover, when a mesotron dies it becomes transformed in part to an electron, and this phenomenon has recently been observed.

To sum up the situation, therefore, we may say that according to beliefs held at any rate until quite recently, two kinds of particles enter our atmosphere from above. First we have electrons, and I include positive and negative electrons. It has been supposed that these particles and their progeny, with the intermediate ghosts, the photons, which come into evidence at each new generation, form the main part of the story of cosmic radiation in the upper regions of the atmosphere and are appreciable in their effects down to altitudes of two or three miles from the earth's surface. Then, we have coming into the atmosphere some other kind of charged particle of non-electron type—probably a heavier particle—a proton, for example, which possesses the power to produce, by a mechanism which we do not yet quite understand, mesotrons, these mesotrons being particles with charges of either sign and each of mass about 200 times that of the electron. We yet lack complete information as to the extent to which these mesotrons are produced almost entirely in the highest regions of the atmosphere or in appreciable part throughout the atmosphere. However this may be, the mesotrons themselves possess the power to pass through considerable thicknesses of material, since they do not lose their energy by the propagation of their species and the sharing of their original store of energy among their progeny as electrons do. Thus, taking only the energy lost by ionization, a mesotron having an energy of twenty billion electron volts could penetrate through the atmosphere and to a further depth comparable with 200 meters of water. An energy such as would be acquired under a potential difference of twenty billion volts is high in terms of our ordinary way of thinking of things, but it is by no means high in the cosmic ray field. Thus, as I have already remarked, an

electron would have to have as much energy as this if it were to reach the earth's atmosphere at all when coming through the earth's magnetic field in the equatorial plane. We have to picture the mesotrons as accompanied at all depths by companion electrons, these electrons having been produced—at the lower depths at any rate—entirely by the process of having been knocked out of atoms by mesotrons or in the act of death of the mesotron, and also, of course, by the subsequent actions of these electrons in giving rise to progeny by the ordinary process of pair formation. Presently, I shall have to return to question the origin of the electrons to be found in the higher regions of the atmosphere, but for the moment we will let the picture stand and inquire as to the nature of the heavy particle or particles which are the parents of the mesotron.

At this point, I should like to give an account of certain speculations and conclusions in which I have been personally interested within the last few years.[1] I have taken as a working hypothesis that whatever the particle may be, such a particle, on entering the atmosphere, breaks up in such a manner that the resulting mesotrons continue to travel along with the velocity which it possessed before the catastrophe. In other words, the assumption is that all that happens is that the heavy particle splits up so that its mass is divided between the mesotrons, and so, consequently, that the velocity of the mesotron is equal to that of the primary. It also follows from this view that the distribution of kinetic energy among the mesotrons will be exactly the same as that among the primary particles except that corresponding energies in the case of the mesotrons will all be divided by N, where N is the number of mesotrons produced by a primary, and therefore the ratio of the mass of the primary to that of the mesotron.

Now it is not to be expected that the mesotrons will all be produced at one altitude. However, if we assume, as seems quite customary in this field, that there is an effective altitude of production—a kind of center of gravity of production—and if we assume tentatively a distribution of energy among the mesotrons, it is possible to work out what is to be expected as regards the variation of mesotron intensity with altitude and with latitude, and to work out, moreover, what is to be expected as regards the energy distribution at sea-level. It is then possible to adjust the assumptions as regards altitude of production and energy distribution so as to harmonize with the facts, and what is most important, it is possible to determine the *lower limit of the kinetic energy* for the mesotrons at the altitude of production for the equator, for

[1] Since this report was presented, these ideas have been developed and extended considerably in a paper, "The Variation of Mesotron Intensity with Altitude and Latitude, Together with Allied Phenomena, and the Bearing of these Matters on the Nature of the Primary Particles" (JOUR. FRANK. INST., **236**, 1, July, 1943, and **236**, 111, August, 1943) and still further in a paper as yet unpublished.

example, and to determine, therefrom, *the lower limit of the velocity of the mesotrons which is also the lower limit of the velocity for the heavy particles.* We can then ask ourselves what mass the heavy particle would have to possess in order that, with this velocity, it could just have penetrated the earth's magnetic field at the equator. The result comes out *equal to the mass of the proton.* I must add that for reasons which I cannot enter into in detail here, the observations used in the above calculations are those at sea-level and at altitudes not above four kilometers, so that we can conclude that the mesotrons observed *at these altitudes* have come from primary particles which are *protons.* I must add that once the idea of a heavy particle came into evidence, others suggested protons as likely candidates for the position, but the object of the calculations above cited was to *determine* the mass of the primary particle and show that the particle is, in actuality, a proton. This matter has some importance, for there is evidence that the proton is not the only primary particle, as will appear later.

And now, having gotten everything nicely settled, I must disturb the equilibrium by suggesting that the electrons in the upper regions of the atmosphere do not come from outside the atmosphere at all, but are born within it, born by the death of the mesotrons which themselves are born from the death of primaries which enter from outside. We shall see, however, that *these* primaries cannot be protons, but particles of greater mass.

And what is the evidence for this disturbing statement as to the origin of the electrons? It is to be found in the fact, as our stratosphere observations have shown, that a large number of the cosmic ray particles to be found in the higher regions of the atmosphere travel in directions making large angles—even a 90° angle—with the vertical. Of course, the effective horizontal thickness of the atmosphere at these altitudes is less than it is at sea-level; but even when allowance is made for this, we can find no justification for supposing that these rays, traveling at large angles to the vertical, can have come from outside the atmosphere.

Again, if the electrons came from outside, we should expect to find that on account of the effect of the earth's magnetic field they would show an asymmetry in intensity with respect to azimuth, whereas our results from the stratosphere flights show symmetry in azimuth to better than one per cent., and the high altitude observations of T. H. Johnson and J. G. Barry, performed near the equator, show no appreciable asymmetry.

If, therefore, the electrons do not come from outside the atmosphere, the only reasonable origin for them is to be found in the death of the mesotrons. Electrons born from mesotrons may be expected to be shot out with equal probability in all directions, as observed from the mesotrons, just as the fragments from a bomb exploded in an airplane would be shot equally in all directions as observed from the

airplane. If the airplane is moving very fast, the fragments will not appear to be shot out symmetrically in all directions as viewed from the ground, but will appear to favor the direction of the airplane. The same thing happens, modified to some degree by the theory of relativity, in the case of the electrons shot out from the mesotrons. If, therefore, we are to have as much symmetry in the ejection of the electrons as is observed from our fixed frame of reference, the mesotrons concerned must be traveling sufficiently slowly. Now if we calculate the results to be expected from the lowest energy mesotrons produced from protons which can enter through the earth's magnetic field, we find that the electrons so produced would not, on the average, deviate enough from the vertical direction to correspond to the facts. We must have mesotrons of lower energy, that is, of lower velocity, and consequently the corresponding primaries must have lower velocities. In this case, the primaries must have greater mass than that of the proton if they are to be able to get through the earth's magnetic field. It turns out that if we assume these primaries to be singly charged helium atoms, the electrons born as their grandchildren (the mesotrons being the parents) would have, in a horizontal direction, an intensity 22 per cent. of the corresponding intensity in the vertical direction at an altitude corresponding to 0.1 atmosphere. Such a result is in harmony with the facts. Mesotrons born with such small energies as would correspond to the velocity appropriate to the helium atoms would have for the most part a life of only about two millionths of a second. They would die before they had traveled more than about 300 meters and their offspring, the electrons, would be born within such a distance of their own place of birth.

The net result of the picture at this stage is, therefore, to the effect that the incoming primary particles are protons and singly charged helium atoms. The former, by their death, give rise to mesotrons which are observed at all altitudes down to sea-level and below. The electron offspring of these mesotrons are also observed at all altitudes. The helium atoms give rise, through mesotrons, to electrons which are confined to the upper regions of the atmosphere, and these yield a considerable intensity in directions inclined at large angles to the vertical. Directly an electron is formed, it proceeds to propagate its species in the manner I have already described, and in doing so, fills the air with ghosts, the photons. That part of the picture remains. We still expect the total radiation to reach a maximum intensity as we ascend to the higher regions of the atmosphere, after which it diminishes, because in the outermost regions there is nothing but the primaries. Indeed, it is possible that there may be more than one maximum in the intensity-altitude curve.

The origin of the primary cosmic rays has always been a matter for profound speculation. One of the earliest suggestions was that of

Professor Millikan to the effect that the cosmic rays arose as photons in a process in which atoms were born in interstellar space by the coming together of the ultimate atomic particles which play a part in their structure. For my own part, I have felt that two mechanisms are available, without too much stretching of the imagination, for the realization of the energies desired. The first of these is one in which charged particles receive their energies in the stars by changing magnetic fields such as we observe in sunspots.

If we take a circular loop of wire and thrust one pole of a magnet through it, we get a current of electricity in the wire. If we keep the magnet still and increase its strength by suitable electrical excitation, then while its strength is increasing a current of electricity will flow around the circular loop of wire. In other words, a changing magnetic field of force represents a region in which electricity becomes set in motion. It is on such principles that a dynamo operates.

Now, it has for long been known that sunspots are associated with intense magnetic activity. The magnetic fields in those spots are continually growing or decaying, and while this is occurring, there are forces which tend to accelerate any electrical charges in the vicinity. It is not so much the magnitudes of the magnetic fields which count as the extent of the regions over which they exist, and it is possible to show that, within the limits of what it is reasonable to assume for changing magnetic fields in stars, charged particle energies can be produced comparable to those observable in the cosmic rays.

Another obvious way of creating high energies is through the operation of processes analogous to those prevailing on earth in the case of a thunderstorm. Even a terrestrial thunderstorm can realize potential differences comparable with a billion volts. Now a thunder shower is simply representative of a huge electrostatic machine operating under the influence of gravity and with its energy supplied by meteorological means. When we think of situations in which, in the novae, a star can blow off 10 per cent. of its substance in a single explosion, or when we contemplate the phenomena taking place in the ordinary stellar mechanisms, it is not difficult to think of situations in which the equivalent of thunderstorms with suitable modifications of detail, and not involving actual rain, can take place in such fashion as to realize potential differences of the order of 20 billion volts or more.

In deciding upon a mechanism suitable for the realization of cosmic ray energies, the difficulty is not so much to find a mechanism which is reasonable, as to decide between the various possibilities and, in fact, to pick out one which is bound up so definitely and inevitably to an accepted stellar or other cosmic process as to leave no doubt, within the realm of reason, and enable us to say not merely that cosmic rays *might* be produced in such and such a manner, but that they *must* be so produced.

Two of the questions which are most frequently asked by the layman are, first, what is the value of studying cosmic rays? and second, can we harness and use the cosmic ray energy? I usually answer the first question by asking another: What is the use of a microscope in medicine and surgery? With a microscope one cannot cure a disease or mend a bone. No, but with a microscope we can learn much concerning bacteriology which has a very fundamental bearing upon the cure of disease and upon the technique of surgery. And so, in the cosmic rays we are presented with activities bound up in most rich and fundamental degree with the fundamentals of the structure of atoms and molecules. Science has reached a stage in which it has exhausted in large degree the potentialities for progress inherent in a general empirical knowledge of the properties of matter. We have reached a stage in which the questions which remain to be answered dig down to the fundamentals of atomic structure; and if ever we are to realize in practical degree such dreams as the utilization of atomic energy, it will be through the aid of greater knowledge acquired by the study of such phenomena as those met with in the cosmic rays that we shall achieve success.

With regard to the cosmic ray energies themselves, while the energy *per unit mass* of each individual ray is very large, the actual energy of a ray is relatively small, and the total energy of all of the rays falling upon us is not very large. A proton cosmic ray, such as could just reach the earth through the magnetic field at the equator, a ray having an energy such that 15 billion volts would be necessary to give it that energy, would in actuality have energy sufficient only to lift a pin's head about a hundredth of an inch. The total mass of all the cosmic rays falling in one second upon the surface of the earth amounts to only about one millionth of one millionth of an ounce, so that in thirty thousand years the weight of the cosmic rays would only increase the weight of the earth by about an ounce.

Speaking in general terms of the energy of cosmic rays as compared with that of sunlight, I have likened the effects of the cosmic rays to that of dropping upon one's head a particle very much smaller than a pin's head once a minute from a distance of a mile, whereas sunlight is to be likened to the dropping upon one's head of a ton of bricks per second from the distance of a foot. The total power supplied by the cosmic rays to the earth is about a million kilowatts. That would be a large amount of power for anyone to pay for, but it is very little as things go in nature. The energy falling on the earth from the sun is about a hundred million times as large, so that he who wishes to tap the power of the universe will do well to look first to that old father of all life, the sun, rather than to those mysterious wasps of space, the cosmic rays.

ON THE EFFICIENCY OF POWER UNITS.

BY

RUPEN EKSERGIAN, Ph.D.

The conversion of heat energy into mechanical work requires (1) an energy balance of the interchange of heat energy and work between parts of the system and (2) a study of the efficiency of the process by a performance balance of the available and unavailable energy components of the system. The latter is important in that it directs the possibility of improvements as well as the proper appraising of any type of existing unit.

The idea of a second law balance is, of course, fundamental in thermodynamic reasoning, dating back to Carnot, Clausius and Thomson. Specific applications to engineering analysis are cited in the comparison of actual engine performance to ideal available vapor cycles as in the Rankine cycle. The Rankine cycle is a component cycle in that it pertains to only one working medium, and measures the availability for work across the engine. On the other hand, thermal efficiencies are frequently calculated, giving the per cent. of work obtained to the heat value of the fuel. The so-called term "boiler efficiency" also illustrates an energy balance, giving the ratio of heat imparted to the steam, to the heat value of the fuel, and accounts for stack losses. However, they in no way indicate the availability of the processes.

Two approaches are made in the literature for an availability balance. One is a direct comparison of the output with an isentropic expansion, while the other has been recently introduced explicitly through the availability equations of Darrieus. In this paper the two methods are shown to be equivalent, and the Darrieus equations are extended to the heat interaction of complex systems. The Darrieus equations state the availability in terms of exit refrigerant temperature. More frequently we are concerned with a limiting back pressure. An extension of the latter is shown in connection with the reheat factor in multi-stage turbines.

In an actual power unit, the heat of combustion is transmitted by radiation and convection to the working medium, and a part is discharged in the exit gases to the atmosphere. Through the working medium, work is performed as in an engine or turbine, and heat at lower temperatures is discharged to a condenser or by exhaust gases directly to the surrounding medium at temperature T_0. Such a process results in an increase of entropy of the system and a corresponding increase of unavailable energy.

The analysis is complicated by different fluid media, such as the combustion gases, the working fluid medium as the water steam flow, and the cooling medium through the condenser.

The circuits for the various fluid media are not always closed paths. It is necessary, therefore, to consider the entrance and exit heat contents or enthalpies of the working fluids.

In the transformation of energy from the entrance or the combustion source to the exit or the refrigerator, the various components and working substances of the system undergo a change of state together with mechanical work performed.

ENERGY RELATIONS.

Let subscript 1 refer to the various entrance states and subscript 2 to the exit states of the system. Let subscript M refer to any one of the fluid mediums, as the combustion gases, or the water-steam flow. Let, further,

Q_1 = heat transmitted externally or generated by combustion, at the source, i.e., $Q_1 = \sum G_m q_{m1}$ (B.T.U./sec.)

Q_2 = heat rejected at the condenser or refrigerator, $= \sum G_m q_{m2}$.

H_{1m} and H_{2m} = entrance and exit enthalpy for any of the fluid media, and defined by

$$H = G[U + Apv] = Gi,$$

where G = lbs. of fluid flow per sec.,
U = intrinsic energy (B.T.U./lb.),
p = pressure at any section (lbs./sq. ft.),
v = specific volume (cu. ft./lb.).

Let

$$P = \text{mechanical work per unit time } \left(\frac{\text{ft.-lbs.}}{\text{sec.}}\right).$$

The overall energy relation for the system is

$$\sum_1^m (H_{1m} - H_{2m}) + \sum_1^m (Q_1 - Q_2) = \sum_1^m AP + \sum_1^m \frac{AG_m}{2g} (C_{2m}^2 - C_{1m}^2), \quad (1)$$

where G_m and C_m are the flow rate and terminal velocity of the several working media m.

AVAILABILITY RELATIONS.

In an adiabatic thermodynamic system with a given source and refrigerator it is well known that the maximum possible mechanical work is obtained through a reversible process, which is characterized by the total entropy of the system which includes both source and refrigerator remaining constant. In any actual process, with the same boundary limitations, the mechanical work is always less than that

corresponding to a reversible path. Such actual systems are irreversible and are characterized by an increase of entropy of the system. The degree of irreversibility, measured by the loss of availability as compared with an ideal reversible transformation, is measured by the lowest available temperature of the system, which usually corresponds to that of the surroundings, times the total increase of entropy resulting in the irreversible process.

The heat energy for any portion of a complex system available for doing mechanical work depends ultimately on the transfer of this energy to a *suitable working medium* in which a pressure head can be established and in which the change in volume in doing mechanical work, is consistent with the geometry suitable for a power unit. In appraising the availability of any portion of the system we can always imagine a possible *reversible* transfer of heat to a suitable working medium for doing mechanical work. It is important to point out that the available energy for doing mechanical work in such reversible transformations, is however, entirely independent of any particular working medium.

In the following analysis, the output of an actual engine with its irreversible path, is *compared* with that of a reversible engine both working between the same source and refrigerator. We will assume both engines to receive the same quantity of heat from the source. Let Q_1 = the heat delivered by the source to the working medium and Q_2 = the heat delivered to the refrigerator from the working medium. Let P = actual work delivered to engine. Let Q_2' = the heat delivered by a reversible engine to the refrigerator. The maximum work delivered to a reversible engine, as in a Carnot cycle, is P_c. Let T_1 = the absolute temperature of the source and T_2 that of the refrigerator.

Then for the actual engine, the energy relation, is,

$$Q_1 - Q_2 = AP,$$

where A is the heat equivalent of mechanical work, while the output of the *reversible engine*, receiving the same quantity of heat from the source, is,

$$Q_1 - Q_2' = AP_c$$

Since the maximum work obtainable is from the reversible engine, hence $AP < AP_c$ and therefore $Q_2 > Q_2'$. The loss of available energy or the increase of unavailable energy *relative to an ideal reversible engine*, is,

$$A(P_c - P) = (Q_1 - Q_2') - (Q_1 - Q_2) = Q_2 - Q_2'$$

and the corresponding relative efficiency, is,

$$\epsilon = \frac{P}{P_c} = \frac{Q_1 - Q_2}{Q_1 - Q_2'} = \frac{AP}{AP + Q_2 - Q_2'}$$

Now, with a reversible engine,

$$\frac{Q_1}{Q_2'} = \frac{T_1}{T_2}, \qquad \therefore \quad \frac{Q_1}{T_1} = \frac{Q_2'}{T_2} = \phi_1$$

Where ϕ_1, is the entropy lost at the source which also equals the gain in entropy at the refrigerator. That is for the ideal reversible engine, there is no change in entropy across the engine. With the same absolute temperatures at source and refrigerator, then, in the actual engine, the entropy at the refrigerator is $\phi_2 = Q_2/T_2$. Hence the increase in entropy with the actual irreversible engine is $\phi_2 - \phi_1$. The increase in unavailable energy is therefore,

$$Q_2 - Q_2' = T_2\left[\frac{Q_2}{T_2} - \frac{Q_2'}{T_2}\right] = T_2(\phi_2 - \phi_1)$$

and

$$\epsilon = \frac{AP}{AP + T_2(\phi_2 - \phi_1)}.$$

Finally, the available energy for doing mechanical work is, likewise,

$$E_{1A} - E_{2A} = Q_1 - Q_2' = (Q_1 - Q_2) + (Q_2 - Q_2')$$
$$\therefore \quad E_{1A} - E_{2A} = AP + T_2(\phi_2 - \phi_1) = (Q_1 - T_2\phi_1) - (Q_2 - T_2\phi_2)$$

where T_2 is the lowest available temperature.

With reference to the surrounding medium at absolute temperature T_0, the total heat energy imparted to a system at temperature T can be divided into two components, the available energy for mechanical work E_A and the unavailable energy E_B.

Thus, in the churning of a liquid of weight W and specific heat C, in raising the temperature from T_1 to T_2, the total amount of work done by the paddle is

$$Q_R = Wc(T_2 - T_1) \quad \text{(B.T.U.)}.$$

In the process of heating the liquid at temperature T, the available and unavailable energy components stored in the liquid for subsequent mechanical work relative to the ambient temperature T_0 are

$$dE_A = \frac{T - T_0}{T} dQ_R = \left(1 - \frac{T_0}{T}\right) cWdT,$$

$$dE_B = \frac{T_0}{T} dQ_R = T_0 cW \frac{dT}{T},$$

and

$$dQ_R = dE_A + dE_B = cWdT.$$

The total increase of the available and unavailable energy components is

$$E_A = cW \int_{T_1}^{T_2} \left(1 - \frac{T_0}{T}\right) dT = cW(T_2 - T_1) - cWT_0 \log_e \frac{T_2}{T_1},$$

$$E_B = T_0 cW \log_e \frac{T_2}{T_1}.$$

Thus, in the churning of the liquid, the loss of available energy for transformation into mechanical work is

$$Q_r - E_A = T_0 cW \log_e \frac{T_2}{T_1} = E_B.$$

IRREVERSIBLE FLOW.

In the flow of fluids with irreversible systems, the mechanical work is always less than the available energy between the entrance and exit terminal sections. The corresponding loss of available energy results in an increase of the unavailable energy of the system. Such losses are accounted for in throttling processes, or in heat transfer between one fluid medium and another. They are characterized by an increase of entropy of the system, while the loss of available energy or the corresponding increase of unavailable energy is measured by the summation of the increases in entropy of the various media times the temperature of the surrounding medium, i.e., the refrigerator temperature.

We can always measure the actual changes of state which occur through an irreversible process, by a reversible path. The heat transferred to the fluid for the reversible path is the total heat, both from external and internal causes,* transferred to the fluid between the terminal sections. The internal heat component is due to the various mechanical losses, regenerated within the fluid into heat. If Q_{12} and Q_R

* Objection to the following line of reasoning is due to (1) in the application of the first law to an energy balance of a system, *only* the external heat appears. In the second law, entropy is regarded as a coördinate and is a function of the thermodynamic state of the system. When external heat is added to a reversible system, then, in general, $d\phi = dQ/T$ is a perfect differential. With irreversible systems, in changing from one state to another, the entropy increases over that of a reversible system with the same external heat. Then, $d\phi > dQ/T$. Therefore, in general $d\phi$ cannot be defined by dQ/T since for irreversible systems dQ/T is *not* a perfect differential.

On the other hand it is entirely permissible to consider the heat required to change the properties of the system actually as they occur. We then apply the "mechanism" of an additional heat "generated internally" to the system so that we arrive at the same change in state as with a reversible path. For an energy balance in the first law, we therefore must also assume a corresponding negative work by friction at the point at which the internal heat is generated. These two aspects cancel each other in considering the overall energy balance.

are the external and internal heat transferred to the fluid, then

$$Q_{21} + Q_R = G\left[U_2 - U_1 + A\int_1^2 pdv\right] = H_2 - H_1 - AG\int_1^2 vdp^* \text{ (B.T.U./sec.)} \tag{2}$$

and the corresponding change in entropy (per pound of fluid) is

$$\phi_2 - \phi_1 = \frac{1}{G}\int_1^2 \frac{d(Q_{12} + Q_R)}{T}.$$

For an adiabatic flow,

$$\phi_2 - \phi_1 = \frac{1}{G}\int_1^2 \frac{dQ_R}{T}. \tag{3}$$

Analysis of Elementary Irreversible System.

Let us first consider an elementary irreversible thermodynamic system consisting of a source and refrigerator at temperatures T_1 and T_2 with a prime mover absorbing mechanical power P. Then if Q_1 is the heat transferred to the working fluid at the source, and Q_2 the heat transferred to the refrigerator,

$$Q_1 - Q_2 = AP. \tag{4}$$

Due to heat transferred at the source, we have a temperature drop $T_1 - T_1'$, where T_1' is the temperature of the fluid at the source. Considering *both* the source and medium, the entropy lost by the source is $\Delta\phi_1 = -\frac{Q_1}{T_1}$ and the entropy gained by the fluid is $\Delta\phi_1' = \frac{Q_1}{T_1'}$. Therefore, due to heat transfer at the source, the net gain in entropy is

$$\Delta\phi_1' + \Delta\phi_1 = \Sigma\,\Delta\phi_1 = \frac{Q_1}{T_1'} - \frac{Q_1}{T_1} = Q_1\left(\frac{T_1 - T_1'}{T_1 T_1'}\right). \tag{5}$$

Across the prime mover, due to friction and throttling losses, the efficiency is *less* than that for the reversible cycle, so that

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1' - T_2'}{T_1'}, \tag{6}$$

$$\left.\begin{aligned}\Delta\phi_2' &= \frac{Q_2}{T_2'},\\ \Delta\phi_1' &= \frac{Q_1}{T_1'};\end{aligned}\right\}$$

hence

$$\frac{Q_2}{T_2'} > \frac{Q_1}{T_1'}, \qquad \therefore \qquad \Delta\phi_2' - \Delta\phi_1' = \Delta\phi_m, \tag{7}$$

so that the medium *gains* entropy $\Delta\phi_m$. We note, since $\Delta\phi_m = 0$ for a *reversible cycle, then* $\Delta\phi_2' = \Delta\phi_1'$, *there being no change in entropy across*

the engine independent of mechanical work being done. This is Carnot's principle for a reversible engine.

In a similar manner, the total gain in entropy due to the heat transfer with temperature drop across the refrigerator is

$$\Delta\phi_2 - \Delta\phi_2' = \sum \Delta\phi_2 = \frac{Q_2}{T_2} - \frac{Q_2}{T_2'} = Q_2\left(\frac{T_2' - T_2}{T_2 T_2'}\right). \tag{8}$$

The total net gain in entropy of the system is

$$\Delta\phi = \sum \Delta\phi_1 + \Delta\phi_m + \sum \Delta\phi_2. \tag{9}$$

Considering the available energy of the source and refrigerator, the net available energy is

$$E_{1A} - E_{2A} = Q_1\left(1 - \frac{T_0}{T_1}\right) - Q_2\left(1 - \frac{T_0}{T_2}\right), \tag{10}$$

where T_0 is the minimum temperature of the surroundings.

A considerable part of this available energy is utilized in doing mechanical work P per unit time. The remaining *loss* of available energy due to the irreversible items already listed, results in an *increase* of the unavailable energy of the system.

$$\therefore \quad E_{1A} - E_{2A} - AP = T_0\Delta\phi, \tag{11}$$

where, from equations (4) and (10),

$$\Delta\phi = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}. \tag{12}$$

Now from (5), (7) and (8) we note (12) can be written

$$\Delta\phi = \left(\frac{Q_2}{T_2} - \frac{Q_2}{T_2'}\right) + \left(\frac{Q_1}{T_1'} - \frac{Q_1}{T_1}\right) + \left(\frac{Q_2}{T_2'} - \frac{Q_1}{T_1'}\right);$$

$$\therefore \quad \Delta\phi = \sum \Delta\phi_2 + \sum \Delta\phi_1 + \Delta\phi_m, \tag{13}$$

so that $\Delta\phi$ accounts for the *total increase of the entropy of the system.*

Since the loss of available energy equals the gain in unavailable energy, we have (noting $Q_1 - Q_2 = AP$)

$$\begin{aligned} E_{1A} - E_{1A}' &= \frac{T_1 - T_0}{T_1} Q_1 - \frac{T_1' - T_0}{T_1'} Q_1 = T_0 \sum \phi_1 \quad \textit{at source,} \\ E_{1A}' - E_{2A}' - AP &= \frac{T_1' - T_0}{T_1'} Q_1 - \frac{T_2' - T_0}{T_2'} Q_2 - AP \\ &= T_0\left(\frac{Q_2}{T_2'} - \frac{Q_1}{T_1'}\right) = T_0\Delta\phi_m \quad \textit{across engine,} \\ E_{2A}' - E_{2A} &= \frac{T_2' - T_0}{T_2'} Q_2 = T_0 \sum \Delta\phi_2 \quad \textit{at refrigerator.} \end{aligned} \tag{14}$$

It is important to note that the loss of available energy across the engine equals the difference between the available energies at entrance and exit sections *minus the work performed per unit time by the engine itself*. On the other hand, where no external work is performed between two sections, the loss of available energy equals the gain in unavailable energy directly.

General Relations in any Thermodynamic System.

Let E_{1A} = the sum of the available energy at entrance corresponding to states 1, i.e., available for mechanical work with respect to the ambient temperature T_0,

E_{2A} = the sum of the exit available energy corresponding to states 2.

Then, the total energy available for mechanical work with respect to the ambient temp. T_0 is $(E_{1A} - E_{2A})$.

Of this total available energy only $\sum P$ is utilized for mechanical work, so that the loss of available energy or the increase of unavailable energy resulting from irreversible losses within the system, such as friction and throttling losses, or losses due to heat transfer from one medium to another, is

$$\sum_1^m (E_{1A} - E_{2A}) - \sum_1^m AP = T_0 \Delta\phi, \tag{15}$$

i.e., *Loss of Available Energy = Increase of Unavailable Energy*, where

$$\Delta\phi = \sum_1^m \left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right) + \sum_1^m G_m(\phi_{2m} - \phi_{1m}).$$

T_0 = temperature of surrounding medium. ϕ_{2m} and ϕ_{1m} = the entropies at terminal sections for medium m. Therefore, the increase of unavailable energy is

$$T_0 \Delta\phi = T_0 \sum_1^m \left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right) + T_0 G_m \sum_1^m (\phi_{2m} - \phi_{1m}) \tag{16}$$

and measures the dissipation of energy in the system.

In a reversible cycle, $T_0\Delta\phi = 0$, so that the total available energy is utilized in the performance of mechanical work.

On combining the overall energy equations (1)

$$\sum_1^m (Q_1 - Q_2) + \sum_1^m (H_{1m} - H_{2m}) = \sum_1^m AP + \sum_1^m \frac{AG_m}{2g} (c_{2m}^2 - c_{1m}^2)$$

with equation (15), we have for the total change of available energy

between the terminal states 1 and 2,

$$\sum_1^m (E_{1A} - E_{2A}) = \sum_1^m \left[\left(H_{1m} - T_0 G_m \phi_{1m} + A G_m \frac{c_{1m}^2}{2g} \right) - \left(H_{2m} - T_0 G_m \phi_{2m} + A G_m \frac{c_{2m}^2}{2g} \right) \right] + \sum_1^m Q_1 \cdot \frac{T_1 - T_0}{T_1} - \sum_1^m Q_2 \frac{T_2 - T_0}{T_2} . \tag{17}$$

It is convenient to express the available energy in terms of a potential function V associated with the medium at a particular state. Then, we define

$$V_{1A} = H_{1m} - T_0 G_m \phi_{1m} \qquad \text{and} \qquad V_{2A} = H_{2m} - T_0 G_m \phi_{2m}$$

so that

$$\Sigma (E_{1A} - E_{2A}) = \Sigma (V_{1A} - V_{2A}) + \sum_1^m Q_1 \frac{T_1 - T_0}{T_1} - \sum_1^m Q_2 \frac{T_2 - T_0}{T_2} + \sum_1^m A G_m \left(\frac{c_{1m}^2 - c_{2m}^2}{2g} \right) , \tag{18}$$

where Q_1 = the heat transmitted from the source at temperature T_1,

Q_2 = the heat rejected to the refrigerator at temperature T_2.

In the case where the heat is added at a varying temperature T, then between temperature limits a and b the available and unavailable components are

$$Q_A = \int_a^b \frac{T - T_0}{T} dQ \qquad \text{and} \qquad Q_B = \int_a^b T_0 \frac{dQ}{T} , \tag{19}$$

where $dQ = (a + bT) G dT$. Obviously, $Q_A = Q - Q_B$.

ANALYSIS OF COMPONENT SYSTEMS.

The preceding equations are applicable to any portion of a system when isolated. In considering component systems separately, we are often concerned with the availability of the process with reference to the particular temperature (or pressure) limits between entrance and exit sections of the given component system. In this case the lowest available temperature corresponds to the lower temperature at the exit section. In general with power units, the limiting temperatures depend on the limiting pressures at the terminal sections.

For an adiabatic expansion and neglecting the kinetic energy term as small, then with $T_2 = T_0$,

$$E_{1A} - E_{2A} - T_2\Delta\phi = AP_{12}, \tag{20}$$

$$H_1 - H_2 = AP_{12}, \tag{21}$$

where

$$E_{1A} = H_1 - T_2G\phi_1, \qquad E_{2A} = H_2 - T_2G\phi_2.$$
$$\therefore \quad \Delta\phi = G(\phi_2 - \phi_1). \tag{22}$$

For an isentropic expansion across the engine, the enthalpy at temperature T_2 and entropy ϕ_1 is related to the actual enthalpy at exit by the equation

$$H_2' = H_2 - T_2G(\phi_2 - \phi_1), \qquad \text{in vapor zone.}$$
$$\therefore \quad E_{1A} - E_{2A} = H_1 - H_2' = AP_{12} + T_2\Delta\phi, \tag{23}$$

where $T_2\Delta\phi = AZ$ = the loss of available energy or the increase of unavailable energy due to throttling and friction losses. The engine efficiency or the efficiency ratio is

$$\epsilon = \frac{AP_{12}}{E_{1A} - E_{2A}} = \frac{AP_{12}}{H_1 - H_2'} = \frac{H_1 - H_2}{H_1 - H_2'}. \tag{24}$$

AVAILABLE ENERGY IN ADIABATIC EXPANSIONS BETWEEN PRESSURE LIMITS.

Since there is no change in entropy in an isentropic expansion, therefore, the maximum mechanical power between given pressure limits is obtained from an ideal isentropic adiabatic expansion. In the preceding equations, the exit temperature was assumed fixed as for a saturated vapor where the temperature is a direct function of the pressure. With superheated vapors for a fixed terminal pressure, the temperature increases with the entropy. For this reason the increase of unavailable energy across a given stage is

$$G\int_1^2 T_{p2}\cdot d\phi = AZ_{12},^* \qquad \text{with} \qquad \Delta\phi = \phi_2 - \phi_1$$

and this results from the heat due to throttling and friction in expanding between pressures 1 and 2, with corresponding increase of entropy from ϕ_1 to ϕ_2.

Therefore, if H_2' is the enthalpy with entropy ϕ_1 (as in an isentropic expansion) at pressure p_2 of the exit section,

$$\left.\begin{aligned} H_1 - H_2' - AZ_{12} &= AP_{12}, \\ H_1 - H_2 &= AP_{12}; \end{aligned}\right\} \tag{25}$$

* The loss of available energy AZ_{12} should not be confused with the internal heat due to friction, i.e., $Q_r = G\int_1^2 Td\phi$, where T is the temp. at which dQ_r is added. T is always higher than T_{p2}, the temp. at exit.

hence

$$\left.\begin{aligned} H_2 - H_2' &= AZ_{12} \\ \text{with} \quad \Delta\phi &= \phi_2 - \phi_1, \end{aligned}\right\} \tag{26}$$

and therefore the engine efficiency is

$$\epsilon = \frac{AP_{12}}{H_1 - H_2'} = \frac{H_1 - H_2' - AZ_{12}}{H_1 - H_2'}. \tag{27}$$

In order to gain some idea of the true efficiency of a locomotive engine, i.e., *for the cylinders alone*, consider a 4–6–2 type with cut-off at 25.5 per cent.

The conditions of the steam at entrance, i.e., in the steam pipe, and at exit, i.e., in the exhaust pipe, are given in the following table:

Pressure (gauge).	Temp.	Superheat.	Enthalpy.	Entropy.
212	748°	356°	$H_1 = 1395$	$\phi_1 = 1.727$
12	361°	117°	$H_2 = 1220$	$\phi_2 = 1.782$

$$H_1 - H_2 = 175, \qquad \phi_2 - \phi_1 = .055.$$

Steam Consumption:

$$\frac{2545}{H_1 - H_2} = \frac{2545}{175} = 14.5 \text{ lbs.}$$

Isentropic Expansion:

$$\left.\begin{aligned} H_1 &= 1395, & H_2' &= 1175, \\ \phi_1 &= 1.727, & \phi_2' &= 1.727. \end{aligned}\right\}$$

Increase of unavailable energy is

$$\begin{aligned} (H_1 - H_2') - AP &= \Delta\phi \cdot T_2, \\ 220 - 175 &= .055(361 + 460). \end{aligned}$$

The cylinder efficiency is

$$\epsilon_c = \frac{AP}{H_1 - H_2'} = \frac{175}{220} = 0.80.$$

Thus the cylinder losses amount to 20 per cent. of *the available energy across the engine.* But these losses have an entirely different ratio and much less effect on the efficiency of the locomotive as a whole.

REHEAT WITH MULTI-STAGE TURBINE (PLATE 1).

Consider a turbine with condenser exit pressure p_n and saturated vapor temperature T_0 with n stages. Let H_1 and H_n be the entrance

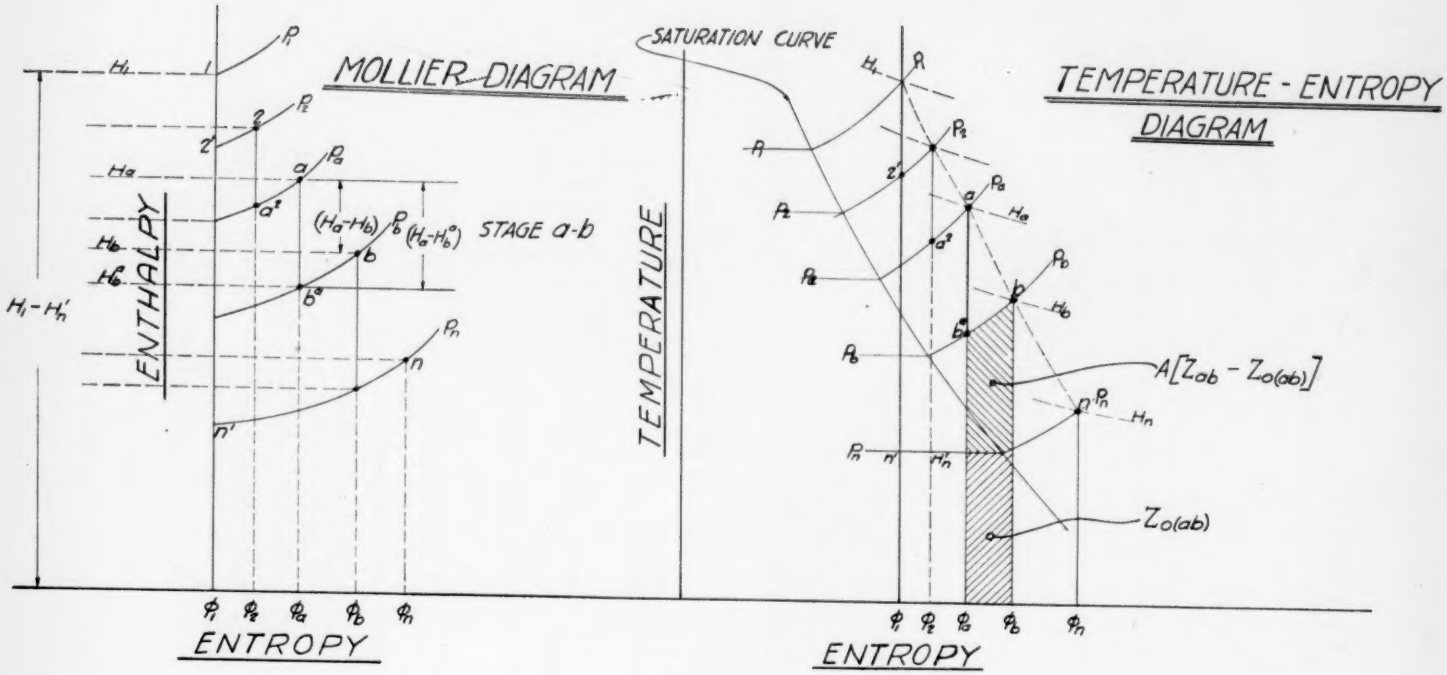

MOLLIER DIAGRAM
ENTHALPY
ENTROPY
STAGE a-b
SATURATION CURVE
TEMPERATURE
TEMPERATURE - ENTROPY DIAGRAM
ENTROPY
A[Zab - Zo(ab)]
Zo(ab)

PLATE I.

and exit enthalpies and H_n' the exit isentropic enthalpy with entropy ϕ_1. Let AZ_0 = the *increase* of unavailable energy over that from an isentropic expansion to the condenser. The corresponding change in entropy is $\Delta\phi_{1n} = \phi_1 - \phi_2$. Then, the availability relation is, for an adiabatic expansion,

$$E_{1A} - E_{nA} = AP + AZ_0,$$
$$H_1 - H_n = AP,$$

which can also be written

$$\left.\begin{aligned} H_1 - H_n' &= AP + AZ_0, \\ H_1 - H_n &= AP, \\ AZ_0 = H_n - H_n' &= G\int_{\phi_1}^{\phi_n} T_{pn}d\phi. \end{aligned}\right\} \quad \text{with} \qquad (28)$$

It is to be noted H_n' is the final exit enthalpy assuming a direct isentropic expansion across the turbine, and T_{pn} is the exit temperature of the working medium at the condenser corresponding to constant pressure p_n. If the discharge is in the saturated zone, then

$$\int_{\phi_1}^{\phi_n} T_{pn}d\phi = T_0(\phi_n - \phi_1).$$

Let $\Delta H_A'' = H_a - H_b{}^a$ be any *isentropic heat drop* across a stage ab, where $H_b{}^a$ is the enthalpy at exit section pressure p_b and entropy ϕ_a. H_a is the enthalpy at entrance section pressure p_a and entropy ϕ_a. Let $\Delta\phi_{ab} = \phi_b - \phi_a$ = the increase in entropy for the actual expansion $H_a - H_b = AP_{ab}$ across the stage, when P_{ab} is the corresponding output. Then for "n" stages,

$$P = \sum_1^n P_{ab}, \qquad \Delta\phi_{1n} = \sum_1^n \Delta\phi_{ab}.$$

For the actual expansion across any stage ab, we have

$$\left.\begin{aligned} H_a - H_b{}^a - AZ_{ab} &= AP_{ab}, \\ H_a - H_b &= AP_{ab}, \\ H_b - H_b{}^a &= AZ_{ab}, \\ \Delta\phi_{ab} &= \phi_b - \phi_a, \end{aligned}\right\} \quad \text{with} \quad \text{per stage.} \qquad (29)$$

Now for each change in entropy $\Delta\phi_{ab} = \phi_b - \phi_a$; then the unavailable energy *at the condenser* is increased by $AZ_{0(ab)}$ and therefore the total increase in unavailable energy for expansion in the n stages is

$$\sum_1^n AZ_{0(ab)} = AZ_0. \qquad (30)$$

On adding $AZ_{0(ab)}$ to both sides of the *stage availability* equation (29)

and summing up for all the n stages, noting the relation (30), we have

$$\sum_1^n (H_a - H_b{}^a) - \sum_1^n A(Z_{ab} - Z_{0(ab)}) = AP + AZ_0. \tag{31}$$

Combining equation (31) with equation (28) we have

$$\sum_1^n (H_a - H_b{}^a) - (H_1 - H_n{}') = \sum_1^n A(Z_{ab} - Z_{0(ab)}) = \sum_1^n AZ_{ab} - AZ_0. \tag{32}$$

When the exhaust to the condenser is in the saturated zone, then, $T_{pn} = T_0$; hence.

$$\sum_1^n (H_a - H_b{}^a) - (H_1 - H_n{}') = \sum_1^n AZ_{ab} - T_0(\phi_n - \phi_1)G. \tag{33}$$

The fact that the available energy $\sum_1^n (H_a - H_b{}^a)$ corresponding to the individual isentropic expansions for the successive stages in a turbine is increased over $H_1 - H_n{}'$ corresponding to a single isentropic expansion across the entire turbine, is due to the additional *available energy component* for any given stage due to the heat of friction in the preceding stages being added at a higher temperature than the condenser temperature.

Let T_{pb} = exit stage temperature at pressure p_b,
dQ_r = internal heat due to friction,
$T_{ab}{}'$ = intermediate temperature within the stage at which dQ_r is added.

Then

$$AZ_{ab} = G\int_{\phi_a}^{\phi_b} T_{pb}d\phi = G\int_{\phi_a}^{\phi_b} T_{pb}\cdot\frac{dQ_r}{T_{ab}{}'}.$$

Therefore,

$$A(Z_{ab} - Z_0) = AZ_{ab} - T_0\Delta\phi_{ab} = \int_{\phi_a}^{\phi_b}\frac{T_{pb} - T_0}{T_{ab}{}'}\cdot dQ_r.$$

With increasing stages $T_{ab}{}'$ approaches T_b; hence

$$\Sigma (H_a - H_b{}^a) - (H_1 - H_n{}') = \sum_1^n \int_{\phi_a}^{\phi_b}\left(\frac{T_{pb} - T_0}{T_{pb}}\right) dQ_r. \tag{34}$$

Since the availability, due to reheat, decreases at the lower stages, it becomes more important to improve the stage efficiency in this region.

Equations (32) and (33) may be written

$$\sum_{1}^{n} \Delta H_a'' = R\Delta H_{1n}', \tag{35}$$

where

$$\Delta H_a'' = H_a - H_b^a, \qquad \Delta H_{1n}' = H_1 - H_n',$$

$$R = 1 + \frac{\sum_{1}^{n} A(Z_{ab} - Z_0)}{H_1 - H_n'} = \text{reheat factor,}$$

where

$$\sum_{1}^{n} AZ_{ab} = \sum_{1}^{n} (H_b - H_b^a) = \sum_{1}^{n} G \int_{\phi_a}^{\phi_b} T_{pb} \cdot d\phi,$$

$$AZ_0 = H_n - H'_{n\phi_1} = T_0(\phi_n - \phi_1)(\text{sat. vap.}).$$

If η_s = the stage efficiency relative to an isentropic heat drop across the stage, and η_t = the turbine efficiency relative to an isentropic heat drop across the turbine, then

$$\sum_{1}^{n} \eta_s \Delta H_a'' = \eta_t \Delta H_{1n}' = AP. \tag{36}$$

Then if η_s is assumed the same for the different stages,

$$\eta_t = \eta_s R,$$

so that the overall efficiency is increased by the reheat factor R.

SINGLE CIRCUIT (PLATE 2).

The Rankine cycle is based on the analysis of the changes of state for the working medium alone through the engine. We are not concerned with the loss of availability in the heat transfer from the boiler gases and radiation, or the loss of availability in the heat transfer at the condenser. The temperatures refer to the temperatures in the working medium only.

The external heat transferred to the isolated circuit consists of the heat Q_1 delivered by the boiler at temperature T_1 and the heat Q_2 rejected to the condenser at temperature T_0. The external work on the circuit consists of the reacting work of the engine $-P$ and the work of the feed pump W_f. The overall energy equation is

$$Q_1 - Q_2 - AP + AW_f = 0. \tag{37}$$

Let A, B and C correspond respectively to the entrance section to the boiler beyond the feed pump, to a section within the boiler at the beginning of the saturation zone and to the exit section of the boiler. Section C also corresponds to the entrance section to the engine, and

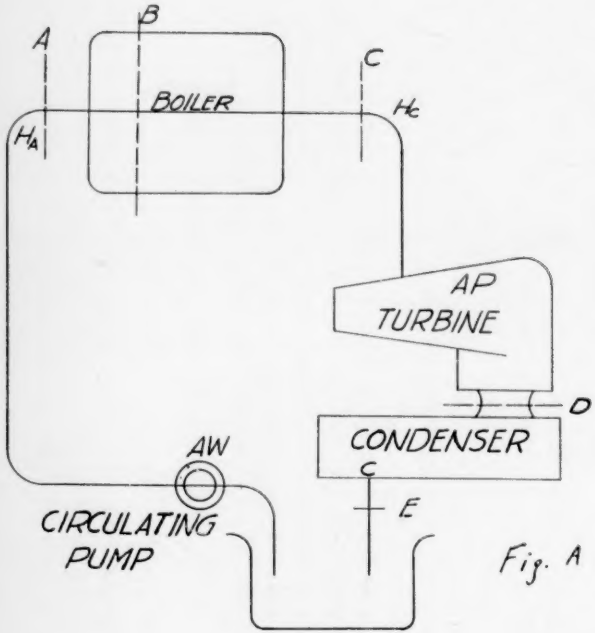


Fig. A

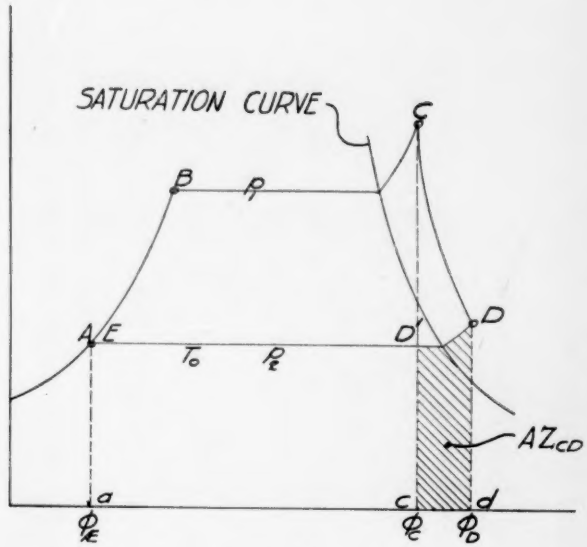


Fig. B

PLATE II.

section D to the exit section of the engine or entrance section to the condenser. The exit section from the condenser to the hot well is E. The feed pump AW_f is located between the hot well and the entrance section to boiler A.

Referring to the temperature entropy diagram, Fig. (b), Plate 2, we note the corresponding states of the fluid at the various sections shown in Fig. (a). With superheated steam at point C, we have an isentropic expansion to the condenser at point D, the actual expansion being to point D at the superheated temperature corresponding to condenser pressure p_2.

The loss of availability across the engine is

$$E_{cA} - E_{DA} - AP = AZ_{cD}, \tag{38}$$

since $H_c - H_D = AP$.

$$E_{cA} - E_{DA} = H_c - (H_D - AZ_{cD}) = H_c - H_D';$$

hence

$$H_c - H_D' = AP + AZ_{cD}. \tag{39}$$

Across the boiler $H_c = H_A + Q_1$ and across the condenser $H_D = H_E + Q_2 - AZ_{cD}$. Across the feed pump we must have $H_A - H_E = AW_f$. Therefore,

$$H_c - H_D' = AW_f + Q_1 - Q_2 + AZ_{cD}, \tag{40}$$

so that the efficiency relative to the available cycle of the engine is

$$\epsilon = \frac{AP}{H_c - H_D'} = \frac{AP}{Q_1 - Q_2 + AW_f + AZ_{cD}}, \tag{41}$$

which is the Rankine cycle efficiency. From the temperature entropy diagram Fig. (b), Q_1 = area $aABCc$, $Q_2 = aADd$, and $AZ_{cD} = cD'Dd$. Hence $Q_1 - Q_2 + AZ_{cD}$ = area $ABCD'$ which is the *available* Rankine heat cycle. The pump work AW_f further contributes to the availability of the engine.

We note from equation (37) the actual work performed is $AP = Q_1 - Q_2 + AW_f$ and this corresponds to the heat cycle area $ABCD' - cD'Dd$ plus the work of the feed pump.

On the Effect of Friction in Fluid Flow Through an Expanding Nozzle (see Appendix, Discussion of Fluid Flow Eqs.).

The effect of friction is twofold: (1) it reduces the velocity and kinetic energy at exit over that corresponding to an isentropic expansion and (2) it increases the thermal properties of the fluid along the expansion. The former is a direct loss of available energy and therefore corresponds to the increase of unavailable energy of the expansion. The latter improves the availability of expansion in that the heat due to friction is added at a higher temperature than the exit temperature. Thus the loss of availability in the expansion is reduced.

The heat generated by friction energy is greater than the loss of kinetic energy because a part of this heat has been transformed into additional mechanical energy along the expansion.

Let $H_1 - H_2'$ = the isentropic heat drop, $H_1 - H_2$ = the actual heat drop, AZ_{12} = the increase of unavailable energy, c_1 and c_2 = the entrance and exit velocities, $dQ_r = AdR$ heat due to friction added along the path, then for G lbs. of flow per unit time, the fundamental equations in the flow through the nozzle are, for an adiabatic expansion,

$$\left.\begin{aligned} H_1 - H_2 &= A\frac{c_2^2 - c_1^2}{2g}, && \textit{energy eq.,} \\ H_2 - H_1 - AG\int_1^2 vdp &= \int_1^2 dQ_r, && \textit{heat eq.,} \\ H_1 - H_2' - AG\frac{c_2^2 - c_1^2}{2g} &= AZ_{12}, && \textit{availability eq.} \end{aligned}\right\} \quad (42)$$

With isentropic expansion, i.e., with no friction losses, the terminal velocity $c_2' > c_2$, where

$$H_1 - H_2' = AG\frac{c_2'^2 - c_1^2}{2g}, \quad (43)$$

which measures the isentropic heat drop in terms of an ideal velocity head. Combining with (a) we have

$$H_2 - H_2' = AZ_{12} = \frac{c_2'^2 - c_2^2}{2g}, \quad (44)$$

which measures the unavailable energy in terms of a velocity head. With an isentropic heat drop the heat equation, since

$$\int_1^2 dQ_r = 0,$$

becomes

$$H_2' - H_1 - AG\int_1^2 v'dp = 0, \quad (45)$$

where v' is the specific volume with an ideal isentropic expansion. On combining (b) and (c),

$$\begin{aligned} H_1 - H_2' + AG\int_1^2 vdp &= AZ_{12} - \int_1^2 dQ_r, \\ \int_1^2 dQ_r - AZ_{12} &= AG\int_2^{'} (v - v')dp. \end{aligned} \quad (46)$$

We note

$$AZ_{12} = G\int_1^2 T_{p_2}d\phi = G\int_1^2 T_{p_2}\frac{dQ_r}{T}, \quad (47)$$

where T_{p_2} is the exit temperature corresponding to exit pressure p_2 and T is the temperature at which dQ_r is added.

$$\therefore \int_1^2 \left(1 - \frac{T_{p_2}}{T}\right) dQ_r = AG \int_2^1 (v - v')dp, \tag{48}$$

which represents the available part of the heat due to friction which in turn increases the specific volume of the fluid over that of an isentropic expansion.

We finally note

$$\begin{aligned} Q_r &= AZ_{12} + AG \int_2^1 (v - v')dp \\ &= A\left(\frac{c_2'^2 - c_2^2}{2g}\right) + \int_1^2 \frac{T - T_{p_2}}{T} dQ_r. \end{aligned} \tag{49}$$

That is, the friction work exceeds the loss of available energy by the additional heat available. This means that only $\frac{A}{Q_r} \cdot \frac{c_2'^2 - c_2^2}{2g}$ of the friction heat is unavailable in the process, or the gain in availability is $\frac{1}{Q_r}\int_1^2 \left(1 - \frac{T_{p_2}}{T}\right) dQ_r$ due to reheat.

OVERALL PLANT EFFICIENCY.

In a complex system with several interacting heat circuits, besides the direct appraisal of individual components previously discussed, it is important to estimate the relative contributions to the unavailable energy of the system. Since we are comparing the percentage of the unavailable energy of any component relative to the total unavailable energy of the system, it is therefore necessary to compare the availability of any component *relative to the lowest temperature of the system* T_0.

It is important always to observe that when heat is added to a circuit or system, the *unavailable energy of the circuit or system increases.* When *heat is abstracted* from a circuit or system, *the unavailable energy of the circuit or system decreases.* Thus in a heat transfer apparatus as in a boiler, the heat transfer from the combustion gases to the steam results in a decrease of unavailable energy for the combustion gas circuit and an increase of unavailable energy to the steam circuit. For the system as a whole the entire heat transfer results in a net gain in unavailable energy since the increase of unavailable energy to the steam circuit exceeds the decrease of unavailable energy of the gas circuit.

In like manner, when heat is rejected from a circuit as in the stack gases for the combustion gas circuit or the exhaust in the steam circuit, there occurs a heat transfer and mixing with the surroundings. The surroundings gain entropy while there is a loss of entropy for the circuit.

Thus if Q_E is the exit heat flow, where T_0 is the temperature of the surroundings and T_n is the temperature of the exhaust medium, then the increase of unavailable energy is

$$GT_0\Delta\phi_E = T_0\int_{T_0}^{T_n}\left(\frac{dQ_E}{T_0} - \frac{dQ_E}{T}\right) = \int_{T_0}^{T_n}\left(\frac{T - T_0}{T}\right)dQ_E,$$

and this equals the loss of available energy in the exit flow to the surroundings.

For an approximate analysis, let the heat components arising from the combustion of a pound of coal be Q_c = the total heat of combustion, Q_r = the radiant energy component, Q_G = the heat delivered to the combustion gases, Q_{sg} = the heat contents in the smoke box gases and Q_s = the heat transmitted to the steam. Also let AP = mechanical work performed per lb. of coal fired, n = lbs. of products of combustion per lb. of coal and r = lbs. of water evaporated per lb. of coal.

For the heat transmitted to the steam,

$$Q_s = Q_c - Q_{sg} = Q_R + Q_G - Q_{sg}, \tag{50}$$

we note $Q_s = H_2 - H_1 = r(h_2 - h_1)$ (per lb. of coal), where h_s and h_f = heat contents of steam and feed water. The radiant energy is

$$Q_r = k\frac{1600}{R}\left[\left(\frac{T_m}{1000}\right)^4 - \left(\frac{T_s}{1000}\right)^4\right] \text{(approx.)},$$

where T_m = flame temperature,
T_s = sat. steam temperature,
R = rate of firing (lbs./sq. H) grate,
k = radiation constant > 1.

For a rough approximation, neglecting the constituent gas components, let

$$c_p = a + bT,$$

where $a = 0.24$, $b = 0.00002$.

Then neglecting direct connection to the steam from the fire box gases, an approximate relation for the total heat generated by combustion is

$$n\int_{T_0}^{T_m}(a + bT)dT + \frac{1600k}{R}\left[\left(\frac{T_m}{1000}\right)^4 - \left(\frac{T_s}{1000}\right)^4\right] = \epsilon_B(\text{B.T.U.})_c, \tag{52}$$

where ϵ_B = boiler eff. $(\text{B.T.U.})_c$ = heat value of coal.
n = lbs. of combustion gas per lb. of coal, which gives a relation between n, T_m and k.

For the heat transferred by convection to the steam in the cooling of the combustion gases,

$$Q_s = (Q_G - Q_{sg}) + Q_r,$$

where

$$Q_G - Q_{sg} = n \int_{T_{sg}}^{T_m} (a + bT)dT$$

$$= \left[a + \frac{b}{2}(T_m + T_{sg})\right](T_m - T_{sg}) \quad (53)$$

and T_{sg} = smoke box temperature.

Availability Relations.

Gas Circuit: In the combustion gas circuit, including the exit surroundings, the increase of entropy is due to (1) the transformation of chemical energy to radiant heat, (2) the transformation of chemical energy to the combustion gases, (3) the heat transfer of the exhaust gases rejected to the surroundings. The decrease of entropy in the gas circuit is due to (4) the abstraction of radiant heat Q_r to the steam and (5) the abstraction of the heat from the combustion gases $(Q_G - Q_{sg})$ to the steam. Items (4) and (5) combined are the gas phase of the heat transfer or the reaction "of the boiler heat transfer on the gas circuit."

Therefore, the total increase in entropy for the gas circuit is

$$\Delta\phi_g = \frac{Q_r}{T_m} + n \int_T^{T_m} (a + bT)\frac{dT}{T}$$

$$+ n \int_{T_0}^{T_{sg}} \left(\frac{1}{T_0} - \frac{1}{T}\right)(a + bT)dT \quad (54)$$

$$- \frac{Q_r}{T_m} - n \int_{T_{sg}}^{T_m} (a + bT)\frac{dT}{T}.$$

Hence, the increase of unavailable energy for the gas steam is

$$T_0\Delta\phi_g = T_0\left[\frac{Q_r}{T_m} + n \int_{T_0}^{T_m} \left((a + bT)\frac{dT}{T}\right)_A\right.$$

$$+ \left[n \int_{T_0}^{T_{sg}} \left(1 - \frac{T_0}{T}\right)(a + bT)dT\right]_B \quad (55)$$

$$\left. - T_0\left[\frac{Q_r}{T_m} + n \int_{T_{sg}}^{T_m} (a + bT)\frac{dT}{T}\right]_C,\right.$$

where A is due to chemical reaction in combustion, B is due to stack gas "loss of *available* energy," and C is due to the heat transfer reaction on the gas circuit.

Steam Circuit: In this circuit, which also includes the exit surroundings, the entropy increases are due to (1) the heat transfer by radiant heat and heat transfer from the combustion gases, which increases the entropy of the steam across the boiler, (2) throttling and friction losses across the engine and (3) the heat transfer losses of the exhaust gases rejected to the surroundings. Now, in the energy balance we find r lbs. of steam per lb. of coal fired, so that for the heat transfer

$$r(h_2 - h_1) = Q_r + n\int_{T_{sg}}^{T_m} (a + bT)dT$$

with a corresponding increase of entropy $\phi_2 - \phi_1$. Let the heat drop across the engine be $r(h_2 - h_3) = AP$, with entropy increase $\phi_3 - \phi_2$. Finally, the heat in the exhaust gases rejected to the atmosphere is $r(h_3 - h_0) = Q_E$.

Therefore, the increase in unavailable energy of the steam circuit is

$$T_0\Delta\phi_s = T_0r[\phi_2 - \phi_1] + T_0r[\phi_3 - \phi_2] - T_0\left\{r[\phi_3 - \phi_0] - \frac{Q_E}{T_0}\right\}. \quad (56)$$

The last term corresponds to a loss of unavailable energy due to the steam leaving the circuit plus a gain due to increase of the unavailable energy to the surroundings. In other words, it corresponds to the exit heat transfer or mixing loss of the exhaust steam to the surroundings.

The total unavailable energy of the system per lb. of coal is

$$T_0[\Delta\phi_s + \Delta\phi_g] = T_0\left\{r(\phi_2 - \phi_1) - \left[\frac{Q_r}{T_m} + n\int_{T_{sg}}^{T_m}(a + bT)\frac{dT}{T}\right]\right\}_1 + \left[n\int_{T_0}^{T_m}\left(1 - \frac{T_0}{T}\right)(a + bT)dT\right]_2 + [Q_E - rT_0(\phi_3 - \phi_0)]_3 + [rT_0(\phi_3 - \phi_2)]_4 + T_0\left[\frac{Q_r}{T_m} + n\int_{T_0}^{T_m}(a + bT)\frac{dT}{T}\right]_5. \quad (57)$$

The component increases of unavailable energy for the several terms on right of above equation are listed below as

1. Heat transfer across boiler heating surface = first term.
2. Stack gas loss of available energy = second term.
3. Exhaust steam, loss of available energy = third term.
4. Throttling and friction losses across engine = fourth term.
5. Combustion chemical energy transformation = fifth term.

The summation of the unavailable energy components must equal the total loss of available energy of the system, that is, the energy due to combustion minus the mechanical work done, per lb. of coal.

On adding the unavailable energy components of the combustion gas circuit, equation (55), we obtain

$$T_0\Delta\phi_g = n\int_{T_0}^{T_{sg}} (a + bT)dT = Q_{sg}. \tag{58}$$

On adding the unavailable energy components of the steam circuit, equation (56) (assuming $\phi_0 = \phi_1$), we have

$$T_0\Delta\phi_s = Q_E. \tag{59}$$

Therefore the total unavailable energy is

$$T_0 \sum \phi = T_0(\Delta\phi_g + \Delta\phi_s) = Q_E + Q_{sg}. \tag{60}$$

The overall availability and energy equations are

$$\left.\begin{aligned} E_{1A} - E_{2A} - AP &= T_0 \sum \phi, \\ Q_c - (Q_E + Q_{sg}) &= AP. \end{aligned}\right\} \tag{61}$$

Hence

$$E_{1A} - E_{2A} = Q_c \tag{62}$$

and the total loss of availability of the system is

$$E_{1A} - E_{2A} - AP = Q_c - AP = (1 - \epsilon)Q_c, \tag{63}$$

where $\epsilon = \dfrac{AP}{Q_c}$, thermal efficiency.

It is to be emphasized in the above analysis we have included the unavailable radiant energy plus the unavailable energy in the combustion gases. That is, we have included the inherent unavailable energy due to chemical reaction, which, therefore, includes the unavailable energy of the source itself as in a Carnot cycle.

Finally, if the availability balance is with respect to the heat value of the coal, then the unavailable components must also include the direct loss due to unburnt fuel going up the stack. On adding heat lost due to unburnt coal $H_c - Q_c$, where H_c is the heat value per lb. of coal, to both sides of the overall availability relation, then

$$H_c = T_0 \sum \phi + AP + (H_c - Q_c), \tag{64}$$

where $T_0 \sum \phi$ is broken down into components already discussed.

AVAILABILITY ACROSS BOILER HEATING SURFACE AND ENGINE.

Let us now consider the *net* available mechanical energy from the combustion source to the terminal sections, at exit to stack of the combustion gases and at exit to exhaust of the steam flow. We are now only including loss of available energy due to heat transfer and across the engine respectively.

For the gas circuit, let Q_c = heat of combustion per lb. of coal, h_{sg} and ϕ_{sg} = the enthalpy and entropy of exit combustion gases to stack, and n = lbs. of gas per lb. of coal. We neglect entrance enthalpy and entropy. The radiant energy per lb. of coal is Q_R. The heat delivered to the combustion gases is

$$Q_c - Q_R = Q_G = n\int_{T_0}^{T_m}(a + bT)dT, \tag{65}$$

where $Q_{sg} = nh_{sg}$ = heat of stack gases, and $Q_R + Q_G - Q_{sg} = Q_s$ = heat transmitted by radiation and convection across heating surface to steam.

For the steam circuit, let h_1 and ϕ_1 = entrance enthalpy and entropy to boiler, h_2 and ϕ_2 = enthalpy and entropy at exit section from boiler or entrance section to engine, h_3 and ϕ_3 = enthalpy and entropy at exhaust section. Then, for r lbs. of steam per lb. of coal,

$$Q_s = r(h_2 - h_1) \qquad \text{and} \qquad AP = r(h_2 - h_3), \tag{66}$$

where AP is the mechanical work done per lb. of coal.

Therefore, in the availability equation,

$$E_{1A} - E_{2A} - AP = T_0\Delta\phi, \tag{67}$$

we have, noting equation (17),

$$E_{1A} - E_{2A} = r(h_1 - T_0\phi_1) - r(h_3 - T_0\phi_3) - n(h_{sg} - T_0\phi_{sg}) + Q_r\left(1 - \frac{T_0}{T_m}\right) + Q_G - nT_0\int_{T_0}^{T_m}(a + bT)\frac{dT}{T}, \tag{68}$$

since

$$n(h_{sg} - T_0\phi_{sg}) = Q_{sg} - nT_0\int_{T_0}^{T_{sg}}(a + bT)\frac{dT}{T}$$

and

$$T_0(\phi_3 - \phi_1) = T_0(\phi_3 - \phi_2) + T_0(\phi_2 - \phi_1);$$

then, the available energy is

$$E_{1A} - E_{2A} = AP + rT_0(\phi_3 - \phi_2) + T_0\left[r(\phi_2 - \phi_1) - n\int_{T_{sg}}^{T_m}(a + bT)\frac{dT}{T} - \frac{Q_r}{T_m}\right]. \tag{69}$$

Hence, the loss of available energy = the increase of unavailable energy is

$$T_0\sum\phi = rT_0(\phi_3 - \phi_2) + T_0\left[r(\phi_2 - \phi_1) - n\int_{T_{sg}}^{T_m}(a + bT)\frac{dT}{T} - \frac{Q_r}{T_m}\right], \tag{70}$$

where the first term on right accounts for engine throttling and the last term for heat transfer loss.

The efficiency of the engine relative to the above available energy is

$$\epsilon = \frac{AP}{E_{1A} - E_{2A}} = \frac{E_{1A} - E_{2A} - \sum T_0 \Delta\phi}{E_{1A} - E_{2A}}.$$

In the analysis of locomotive, it has been shown that with a thermal efficiency of 7 per cent. or 980 B.T.U. per pound of coal for mechanical work, the loss of available energy due to heat transfer in the boiler is in the order of 3,400 B.T.U. while the throttling loss across the engine is 280 B.T.U. per pound of coal. This shows the importance of raising the temperature of the working medium which in turn requires high pressures.

From a practical point of view a basic limitation for increasing the availability of a power unit is the limitations of a suitable working medium consistent in the desirable design proportions of a power unit. With steam the rapid rise in pressure with temperature in the saturated zone which is capable of retaining large heat values per pound of fluid, limits the available temperatures. In addition effective heat transfer requires larger heating surface with lower temperature gradients or greater mass velocities. All these impose limitations on weight and size of apparatus.

APPENDIX ON THE EQUATIONS OF FLUID FLOW.

For the steady flow of fluids, we have four fundamental relations, (1) a mechanical or momentum relation, (2) an overall energy equation, (3) the heat equation which measures an irreversible process by a reversible path, in which we are concerned only with the properties of the fluid at the terminal sections, and, finally, (4) the continuity equation. In general, only two of the equations (1), (2) and (3) are independent; either one can be derived from the other two.

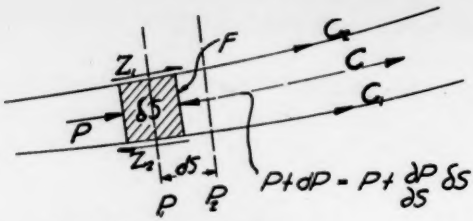
1. MECHANICAL OR MOMENTUM RELATIONS.

(a) Bernoulli's Equation (Figs. 1 and 2, Plate 3).

Consider an element of a fluid tube AB, of volume $F \cdot \delta s$, moving along path s. The equation of motion at any section F, with perimeter P, density ρ and velocity c, along the path s, is

$$\frac{\rho F \delta s}{g}\left(\frac{\partial c}{\partial t} + c\frac{\partial c}{\partial s}\right) = -F\frac{\partial p}{\partial s}\delta s - dZ, \qquad (1)$$

$$Z_2 - Z_1 = dZ = \frac{\xi\rho}{2g} c^2 P \delta s = \text{friction on element.}$$



$\rho = \frac{1}{V}$ = DENSITY (LBS/CU FT.)
C = VELOCITY (FT./SEC.)
$\frac{dC}{dt} = \frac{\partial C}{\partial t} + C\frac{\partial C}{\partial S}$ = ACCELERATION (FT/sec.²)

FIG. 1.

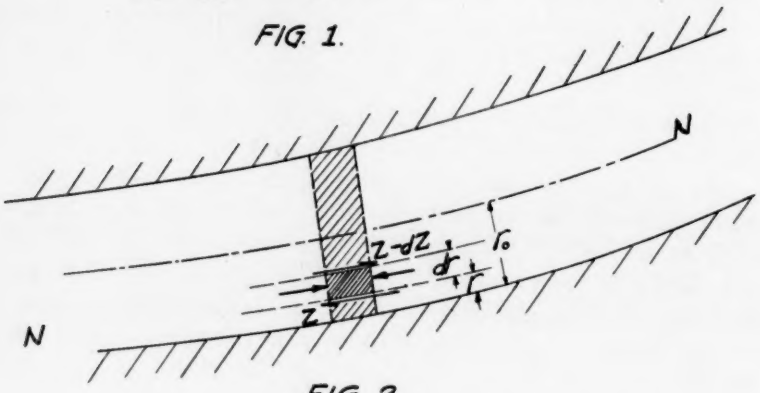
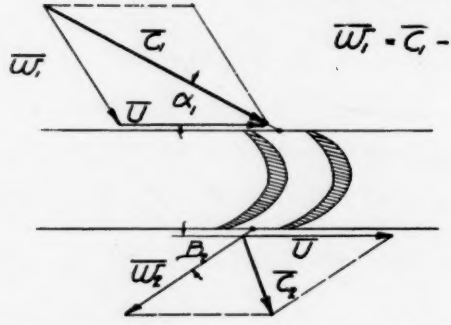


FIG. 2.

G = MASS FLOW (LBS/SEC)
$\overline{C_1}$ = ABSOLUTE ENTRANCE VELOCITY
$\overline{W_2}$ = RELATIVE EXIT VELOCITY
$\overline{U}$ = PERIPHERAL VELOCITY
r = RADIUS OF WHEEL



$\overline{W_1} = \overline{C_1} - \overline{U}$

$\Phi_s = \frac{G}{g}[C_1 \cos\alpha_1 - (U - W_2 \cos\beta_2)]r$

= TORQUE PER STAGE

FIG. 3.

PLATE III.

Since $\rho = \frac{1}{v}$, where v = specific volume,

$$m = \frac{F}{P} = \text{the hydraulic radius} \left(= \frac{d}{4} \text{ for pipe} \right).$$

$$\xi = f(R_\rho) = f\left(\frac{\rho c^2 d}{\mu}\right), \text{ a function of the Reynold's number}$$

μ = coeff. of viscosity.

For steady flow, $\frac{\partial c}{\partial t} = 0$, therefore eq. (1) reduces to

$$\left.\begin{aligned} \frac{cdc}{g} &= -vdp - \frac{\xi}{m}\frac{c^2}{2g}ds \\ \text{or} \qquad \frac{c_2^2 - c_1^2}{2g} &= -\int_1^2 vdp - \int_1^2 \frac{\xi}{m}\frac{c^2}{2g}ds. \end{aligned}\right\} \qquad (2)^*$$

It is to be noted that either the differential or integrated form can be regarded as a mechanical work equation.

(b) Mechanical Output.

When considering the interaction of the fluid flow and the rotor of a turbine, the rate of energy transfer is

$$P = \Phi\omega \qquad (3) \qquad \text{where} \begin{cases} \Phi = \text{torque on rotor,} \\ \omega = \text{ang. vel. of rotor.} \end{cases}$$

This energy transfer has two aspects. When considering the fluid flow,

* The internal work due to friction is $\int Z \cdot \delta c \cdot dt$. The work done on the element is $-\delta(Zc)dt$. For a *flux* of fluid flow containing a family of tubes, bounded by a stationary wall as in a channel or pipe, where r_0 is the radius of channel, we find

$$\int_0^{r_0} \delta(Z \cdot c)dt = \int_0^{r_0} (Z\delta c + c\delta Z)dt = 0$$

since

$$\int_0^{r_0} \delta(Zc)dt = [(Zc)_{r_0} - (Zc)_0]dt = 0.$$

$c = 0$, when $r = 0$, and $Z = 0$ due to symmetry, when $r = r_0$. Therefore,

$$\int_0^{r_0} Z\delta c \cdot dt = -\int_0^{r_0} c\delta Z \cdot dt = -\int_0^{r_0} \delta Z \cdot ds.$$

Therefore, the contribution of the *internal friction energy per tube* of the flow is $\delta Z \cdot ds$. The internal friction energy per unit weight along the tube is

$$\delta R = \frac{\delta Z \cdot ds}{\rho F \cdot ds} = z \cdot ds = \frac{\xi}{m}\frac{c^2}{2g} \cdot ds,$$

$$R_{12} = \int_1^2 \frac{\xi}{m}\frac{c^2}{2g} \cdot ds.$$

Since the *total energy* of the fluid flow is unaffected by friction, evidently AR must reappear as internal heat energy Q_r. That is, $Q_r = AR$.

it is the work of the moving blades reacting on the flow. When considering the rotor, it is the work on the rotor due to the reaction of the fluid. The rate of energy transfer P is measured either by the tangential reaction component, due to the interaction between fluid and rotor, times the peripheral velocity of the rotor or, more generally, by the torque times the angular velocity of the rotor.

The torque interaction between fluid and rotor is equal to the rate of change of the angular momentum of the fluid due to this interaction and is, therefore, the change in angular momentum of the fluid from the entrance to the exit sides or vice versa. The entrance angular momentum is determined by the tangential velocity from the stationary blades, whereas the exit angular momentum is determined by the absolute whirl velocity from the moving blades. When the entrance angular momentum to the moving blades exceeds the exit angular momentum, the torque reaction of the rotor opposes the flow, while the action on the rotor drives the rotor, and the energy transfer corresponds to that of a turbine. When the exit angular momentum exceeds the entrance, work is done on the flow, with a corresponding resistance to the motion of the rotor. In this case we have a pump.

Referring to Fig. 3, the torque exerted on the moving blades of a turbine stage is

$$\Phi_s = \frac{G}{g}[c_1 \cos \alpha_1 - (u - w_2 \cos \beta_2)]r(\text{lb.-ft.}), \tag{4}$$

where G/g is the mass flow of the fluid per unit time, c_1 = the absolute entrance velocity at entrance angle α_1, $u = \omega r$ = peripheral velocity of blades, w_2 = the relative exit velocity at relative exit angle β_2 to the rear and r = the blade rim radius.

2. OVERALL ENERGY RELATIONS: STEADY FLOW.

The work done by the terminal pressures per lb. fluid flow is $p_1v_1 - p_2v_2$, where p_1 and p_2 are the end pressures, and v_1 and v_2 are the corresponding specific volumes. The change in internal intrinsic energy is $u_2 - u_1$ and the change in kinetic energy is $\frac{1}{2g}(c_2^2 - c_1^2)$, per lb. of flow. If Q is the heat added *externally* to the flow path, then with G lbs. of flow per unit time,

$$JQ + (p_1v_1 - p_2v_2)G - P = JG(U_2 - U_1) + \frac{G}{2g}(c_2^2 - c_1^2).$$

$$\therefore \quad Q + H_1 - H_2 - P = \frac{AG}{2g}(c_2^2 - c_1^2), \tag{5}$$

where $H = G(Apv + U)$ = Total enthalpy at a given section,
P = Mechanical energy transferred at turbine.

Since the heat generated internally through friction, Q_r, is identical to the corresponding work of friction AR, these terms cancel out and do not appear explicitly in the energy equation. On the other hand, indirectly, the work of friction, throttling losses, etc., result both in the increase of intrinsic energy and specific volume at the exit section but with a corresponding decrease in the exit velocity. That is, the enthalpy is increased at the exit section, thus cutting down the total head $H_1 - H_2$, resulting in a decrease in the exit kinetic energy.

Applications to Turbine Stage.—Adiabatic Heat Drop.

The mechanical power developed per stage is

$$P_s = \Phi_s \omega = \frac{G}{g}[c_1 \cos \alpha_1 + w_2 \cos \beta_2 - u]u \left(\frac{\text{ft.-lbs.}}{\text{sec.}} \right), \qquad (6)$$

where ω = ang. vel., $\omega r = u$ = peripheral velocity. Since

$$\bar{w}_1 = \bar{c}_1 - \bar{u} \qquad \text{and} \qquad \bar{c}_2 = \bar{u} + \bar{w}_2,$$

then

$$w_1^2 = c_1^2 + u^2 - 2c_1 u \cos \alpha_1,$$
$$c_2^2 = w_2^2 + u^2 - 2w_2 u \cos \beta_2;$$

therefore,

$$P_s = \frac{G}{g}[(c_1^2 - c_2^2) + (w_2^2 - w_1^2)] \left(\frac{\text{ft.-lbs.}}{\text{sec.}} \right). \qquad (7)$$

It is important to note that while β_2 is the blade exit angle of the moving blades, β_1 in general, due to shock losses at entrance, does not coincide with the entrance blade angle of the moving blades. For this reason the relative velocity at entrance is obtained from the vector relation $\bar{w}_1 = \bar{c}_1 - \bar{u}$.

Whether for impulse or reaction stages, the heat drop $H_1 - H_2$ *across a rotating wheel* is obtained from the energy equation

$$-AP_s + H_1 - H_2 = \frac{AG}{2g}(c_2^2 - c_1^2); \qquad (8)$$

$$\therefore \quad H_1 - H_2 = \frac{AG}{2g}(w_2^2 - w_1^2) \text{ per stage.} \qquad (9)$$

That is, the heat drop across the moving blades is equal to the change in the kinetic energy in terms of the *relative* velocities with, however, w_1 defined as above.

3. THE HEAT EQUATION.

In this equation we are only concerned with the changes of state for any portion of the fluid between any two sections in the flow. Since

entropy is a property of the state of a fluid, changes in entropy can be measured by a reversible path. The element receives from external sources the heat dq_{12} and in addition the heat AdR_{12} generated by friction at temperature T. We can isolate a fluid element and compare a reversible path with the same changes of state that occur from point to point along its actual path. Now the change in entropy due to the total heat applied to the element is

$$d\phi = \frac{dq_{12} + AdR_{12}}{T},$$

but the corresponding change of entropy of the element measured by *a reversible path* consistent with the actual changes of state along the path is

$$d\phi = \frac{dU + Apdv}{T}.$$

Therefore the heat required to change the state of the element along its path is

$$dq_{12} + AdR_{12} = dU + Apdv \text{ (per lb. of flow).} \tag{10}$$

The above heat equation is an independent relation. It can, however, be derived by combining the equation of energy and the equation of momentum. Noting that the heat energy, arising from friction per lb. of fluid flow, is

$$AdR_{12} = \frac{A \cdot \delta Z \cdot ds}{\rho F ds} = A \frac{\xi}{m} \frac{c^2}{2g} \cdot ds,$$

where we define $dQ_r = AGdR_{12}$, for G lbs. of flow per unit time.

The motion of the c. of g. of the element is

$$\frac{\rho F \delta s}{g} \cdot c \frac{dc}{ds} = -Fdp - dZ,$$

or

$$\left.\begin{aligned} \frac{d(c^2)}{2g} &= -\frac{dp}{\rho} - dR_{12}, \\ \frac{d(c^2)}{2g} &= -vdp - dR_{12}, \end{aligned}\right\} \tag{11}$$

and the energy equation is

$$dq_{12} - Ad(pv) = dU + A\frac{d(c^2)}{2g}. \tag{12}$$

On combining (11) and (12) we obtain equation (10). For this reason the heat equation can also be regarded as the equation of energy relative to the c. of g. of the moving element.

ACKNOWLEDGMENT.—The author is indebted to William H. Miller for his material aid in the preparation of this paper.

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Quartz Crystals.—Quartz crystals are urgently needed in large quantities for making quartz crystal oscillator plates used in radio equipment for the armed forces. At present all of the quartz used for this purpose comes from Brazil. This supply is not sufficient, however, and it is necessary to find and develop further sources in the United States.

There is no difficulty in finding low grade quartz. Quartz is perhaps the world's commonest mineral. It is found abundantly as boulders and pebbles or as veins and grains in granite and other rocks. But the large clear quartz crystals required for radio purposes are not common at all, though they do occur in some places lining cavities in rock, and in the dirt and gravel nearby.

Only separate, individual crystals are wanted—not groups or clusters or grainy masses. Each separate crystal must weigh at least one-half pound. Measured in inches, the crystals must be at least an inch thick and three inches long. Crystals with natural faces are preferred but crystals with all the faces broken off can still be used. The above sizes are the smallest that can be used. Larger sizes, between one and four pounds, are preferred.

Each crystal must be clear and colorless on the inside. Clear means clear as glass, perfectly clear and transparent, so that a newspaper can be read through the crystal. It is not necessary that the whole crystal be perfect, but large portions of the crystal must be perfect, and these are the parts which are cut out and used. These parts must be entirely free from specks, bubbles, and lines on the inside, absolutely free from clouds, cracks and flaws of any kind. These parts must be at least as large as walnuts. Furthermore the bad portion of the crystal must not be more than twice the volume of the perfect portions. The reason for this is that it would not pay to do too much sawing in order to cut away the bad part of the crystal from the perfect part. Quartz crystals are often good near the pointed end but bad at the base end. In this case the bad end can usually be knocked off carefully with a hammer so that the remaining crystal is mostly good. Some crystals which appear to be perfect are useless because of the optical twinning, but this is determined only with special equipment.

Colored quartz is not wanted. Milky quartz, purple quartz (amethyst), rose quartz cannot be used. The only exception is that light smoky quartz can be used, otherwise quartz must be colorless.

The outside of the crystal does not matter except that it is necessary to look through the crystal in order to see flaws on the inside. Some quartz crystals are covered with iron stain but this can be removed and does no harm.

Anyone who owns or knows of a location where such material can be produced in quantity is requested to send a sample consisting of several of the best crystals he can select to the Miscellaneous Minerals Division, War Production Board, Temporary "R" Building, Washington, D. C.

R. H. O.

SOLUTION THEORY AND pH MEASUREMENTS.

BY

P. G. NUTTING.

Since the advent of the sensitive and easily operated glass electrode for pH measurement in the investigation of solutions, a number of phenomena have been observed which indicate that some revision and extensions of solution theory may be advisable. Potentials determined with a pH meter are generally taken to be a measure of the hydrogen ion concentration in the solution contacted, yet many observers are convinced that in many cases it is not. Certain acid solutions become more acid when alkali is added. Many solutions give from two to six perfectly definite and repeatable pH readings, some of which do not vary with dilution. Most simple salt solutions show a linear relation between pH and log concentration over a wide range. Adsorption has been shown to be a linear function of pH. It is of interest to know whether deductions from exact fundamental solution theory are consistent with these observations and how they are to be interpreted.

The foundations of solution theory were developed and coördinated fifty years ago, chiefly by Kohlrausch in the field of electrolytic conduction, by Nernst with his theory of concentration potential and by the thermodynamic treatment of Arrhenius. The unit of potential was the volt and the zero of potential, which is arbitrary, was taken as that of the hydrogen saturated platinum electrode in hydrogen at one atmosphere. According to Nernst, the potential of an electrolytic cell is due entirely to the net concentrations of ions at the interface, caused by differences in the solution pressures of the ions. Very little has been added to the fundamental theory.

Sörenson about 1907 introduced the more open pH scale for practical work, such that 1 volt equals about 16 pH units. The pH scale is such as to give pH = 7 in water with no ions other than H and OH present. Hence H = OH in concentration and therefore $H \times OH = 10^{-14}$ when H and OH are expressed in moles per liter, pH = $-\log H$ by definition and the temperature is 24.9° C. Though very convenient for rough practical work, the Sörensen scale cannot be precisely defined without assumptions. Nor can it be checked with high precision against an instrument such as the hydrogen electrode because of the reference electrode required for manipulating the latter and its lack of sensitivity. The Bureau of Standards is now engaged in a calibration of the pH scale, and the development of specifications for reference solutions.

EXACT RELATIONS IN SOLUTION THEORY.

A salt AB, a combination of an acid A with a base B, when dissolved in water partly dissociates into ions A and B. Each anion A associates with an H from the water to form the free acid HA which in turn partly dissociates into free ions H and A. Similarly the cation B forms free base BOH which redissociates into B and OH as shown in the marginal printed sketch. Water can supply H and OH indefinitely. Given the amounts of salt and water, what are the amounts of each of the four ions present and their relation to the four undissociated molecules?

AB
A B
HA BOH
H OH
HOH

Letting the symbols represent molar concentrations and C that of the salt dissolved, then evidently

$$C = AB + HA + A = AB + BOH + B. \tag{1}$$

Hence

$$HA + A = BOH + B, \tag{1a}$$

$$HA + H = BOH + OH, \tag{1b}$$

$$A + OH = B + H. \tag{2}$$

(2) is the condition for electrical neutrality. Only two of these three equations are independent since any one of them may be obtained from the other two.

After a solution has reached equilibrium, the mass law gives the relations between each of the four undissociated residues AB, HA, BOH and HOH and the pair of ions into which each is partly dissociated.

$$A \cdot B = K_s AB, \tag{3}$$

$$A \cdot H = K_a HA, \tag{4}$$

$$B \cdot OH = K_b BOH, \tag{5}$$

$$H \cdot OH = K_w HOH. \tag{6}$$

The mass law constants K_s, K_a, K_b, and K_w are accepted as in fact invariant since they may be shown to be constant by thermodynamic potential theory. They are measures of the energy of association (RT log K) of the ions of each pair. Relations (1) and (2) are exact and the mass laws (3) to (6) are, for the present, given the same status. However, none of them takes any account of the absorption of ions on walls, solid particles in suspension or other nondiffusible matter which in some cases seriously affects concentrations and pressures and requires the application of the Donnan principle. The mass laws (3) to (6) must be modified for strong solutions for they assume unit ionic activity and molecular activities included in the K constants.

These six relations are insufficient to determine the seven unknowns which they contain so that an additional datum (usually electrical resistance or potential) is required. However, they may be solved to give any one variable in terms of H and the constants. The substitution of HA and BOH from (4) and (5) in (1a) gives the fundamental relation between the four ions.

$$A\left(\frac{H}{K_a}+1\right)=B\left(\frac{OH}{K_b}+1\right). \tag{7}$$

The independent exact relation $A + OH = B + H$ with (7) may be solved for A and B in terms of the water ions H and OH;

$$A\left(\frac{H}{K_a}-\frac{OH}{K_b}\right)=(OH-H)\left(\frac{OH}{K_b}+1\right) \quad \text{or} \tag{8}$$

$$A=\frac{K_w-H^2}{H^2-R}\left(\frac{R}{H}+K_a\right),$$

$$B\left(\frac{H}{K_a}-\frac{OH}{K_b}\right)=(OH-H)\left(\frac{H}{K_a}+1\right) \quad \text{or} \tag{9}$$

$$B=\frac{K_w-H^2}{H^2-R}(H+K_a),$$

in which $R = K_aK_w : K_b$ for brevity. Both $A = 0$ and $B = 0$ for $H = OH$ (which is the same as $H^2 = K_w$) since K_a and K_b are never equal. At the other limit $H^2 = R$ or $H/K_a = OH/K_b$ and $A = B$.

None of the variables or constants (A, H, R, etc.) in (8) and (9) can be negative, hence $K_w - H^2$ and $H^2 - R$ must always have the same sign, either both positive or both negative. In an acid solution $K_w < H^2 < R$, $H > OH$, $A > B$, $2pH < 14$. In an alkaline solution $K_w > H^2 > R$, $H < OH$, $A < B$, $2pH > 14$. In other words, the pH of a solution may range from $2pH = pK_w$ up or down to $2pH = pR = pK_a - pK_b + pK_w$. The fraction $(K_w - H^2) : (H^2 - R)$ is always positive and finite, as are the following parentheses. The limiting cases $H^2 = K_w$ and $H^2 = R$ are of no practical interest; the first means an empty solvent, the second requires $K_a = K_b$ but these dissociation constants are never equal.

Relations between free acid (HA) or free base (BOH) and H are easily obtained from (8) and (9). Calling the fractional part Q,

$$A=Q\left(\frac{R}{H}+K_a\right), \qquad HA=Q\left(\frac{R}{K_a}+H\right), \tag{10}$$

$$B=Q(H+K_a), \qquad BOH=Q\left(\frac{R}{K_a}+\frac{R}{H}\right). \tag{11}$$

Hence $HA - BOH = Q\left(H - \frac{R}{H}\right)$, and $HA = BOH$ for $H^2 = R$ which is the condition for A = B.

Equations (8) to (11) give the molar concentrations of anions, cations, free acid and free base in terms of H and the dissociation constants. If the latter are known and H is obtained from the observed pH, then the ionic concentrations may be computed for these equations. Solving (1b) and (2) in similar manner gives H in terms of A (or B) and constants. This whole group of *titration* equations is of interest in showing what to expect in special cases, such as H^2 nearly equal to K_w or to R, R very large or very small.

The four buffer equations, also in general and exact form, are readily obtained by taking logarithms of (8) to (11) and differentiating, making use of the logarithmic differential of (3) to (6). For the addition of

(12) salt, AB, by (3), $\frac{d\mathrm{AB}}{\mathrm{AB}} = \frac{d\mathrm{A}}{\mathrm{A}} + \frac{d\mathrm{B}}{\mathrm{B}}$,

(13) free acid, HA by (4), $\frac{d\mathrm{HA}}{\mathrm{HA}} = \frac{d\mathrm{A}}{\mathrm{A}} + \frac{d\mathrm{H}}{\mathrm{H}}$,

(14) free base, BOH, by (5), $\frac{d\mathrm{BOH}}{\mathrm{BOH}} = \frac{d\mathrm{B}}{\mathrm{B}} - \frac{d\mathrm{H}}{\mathrm{H}}$,

since $d\mathrm{OH} : \mathrm{OH} = -d\mathrm{H} : \mathrm{H}$. Equations (8) and (9) give

(15) $$\frac{d\mathrm{A} : \mathrm{A}}{d\mathrm{H} : \mathrm{H}} = -\frac{2\mathrm{H}^2}{\mathrm{K}_w - \mathrm{H}^2} - \frac{2\mathrm{H}^2}{\mathrm{H}^2 - \mathrm{R}} - \frac{\mathrm{R}}{\mathrm{R} + \mathrm{HK}_a},$$

(16) $$\frac{d\mathrm{B} : \mathrm{B}}{d\mathrm{H} : \mathrm{H}} = -\frac{2\mathrm{H}^2}{\mathrm{K}_w - \mathrm{H}^2} - \frac{2\mathrm{H}^2}{\mathrm{H}^2 - \mathrm{R}} + \frac{\mathrm{H}}{\mathrm{H} + \mathrm{K}_a}.$$

Substitution in (12) to (14) gives the buffer equations sought. The fractional change in H caused by additional salt AB is given by

(17) $$\frac{d\mathrm{AB} : \mathrm{AB}}{d\mathrm{H} : \mathrm{H}} = -2\mathrm{S} - \frac{\mathrm{R}}{\mathrm{R} + \mathrm{HK}_a} + \frac{\mathrm{H}}{\mathrm{H} + \mathrm{K}_a},$$

for free acid, HA,

(18) $$\frac{d\mathrm{HA} : \mathrm{HA}}{d\mathrm{H} : \mathrm{H}} = -\mathrm{S} + \frac{\mathrm{HK}_a}{\mathrm{R} + \mathrm{HK}_a},$$

while for additional free base BOH,

(19) $$\frac{d\mathrm{BOH} : \mathrm{BOH}}{d\mathrm{H} : \mathrm{H}} = -\mathrm{S} - \frac{\mathrm{K}_a}{\mathrm{H} + \mathrm{K}_a}.$$

S for brevity, has been written for the two terms common to (15) and (16). The fourth buffer equation for dilution, is (17) with reversed sign. The substitution $dp\mathrm{H} = -0.4343d\mathrm{H} : \mathrm{H}$ gives the buffer equations in terms of pH if desired.

Consider a very dilute alkaline solution being titrated with very dilute acid. H^2 is slightly less than K_w at the start, so that S is positive and (18) $= -\mathrm{S} + \mathrm{HK}_a : (\mathrm{R} + \mathrm{HK}_a)$ at the start of titration and remains negative until near neutralization. The pH at first increases, then decreases. Conversely, in a very dilute (or but slightly dissociated) acid solution S is negative and large at the start and the first addition of alkali makes it more acid. At the time observations of this nature were recorded [1] they could not be explained but the exact buffer equations above (since derived) indicate that they are to be expected.

When a solution is diluted in steps of ten and the pH of each dilution plotted against log concentration, the graph is a straight line over a wide range provided no second hydrogens are dissociated. As the line approaches pH = 7 (10^{-7} to 10^{-9} molar) it turns to join it as asymptote. At high concentrations (one per cent. or higher) the pH line again turns toward horizontal. In other words $\mathrm{pH} = a \log \mathrm{C} + b$ (where C is concentration) over a wide range. The constant a is negative for acids ($a = -1$ for HCl), positive for bases ($a = +1$ for KOH), intermediate for salts. For pure silica solution $a = -.045$, for FeOOH $a = +.07$, for KCl + .30. Both a and b may be quickly determined with considerable precision with a good pH meter. They are characteristics of a solution of evident importance; how are they to be interpreted?

The fundamental equations (1) and (2) solved for H in terms of C give relations so complex as to be useless. However, the free energy relations, with constant temperature and volume, are simple and easily interpreted. For two components, the partial derivatives of the Gibbs equation of chemical potential give

$$(20) \qquad \frac{d \log \mathrm{M}_2}{d \log \mathrm{M}_1} = \frac{\mathrm{M}_1 e_1}{\mathrm{M}_2 e_2} = a = \frac{d\mathrm{E}_2}{d\mathrm{E}_1},$$

in which M is molar concentration, e the energy required to convert unit mass and E chemical energy per mole. When the observed variables are H and C, a lies between +1 and −1. At those limits the energies are equal, either direct or reverse. For silica solution ($a = -.045$), evidently the mass ratio is low on account of the low dissociation of silicic acid. For KCl solution both hydrolysis and specific energy are factors. However, such minor variants as that of the partial molal free energy of the water itself are not taken into consideration and (20) is useful chiefly for orientation. The constant b in

[1] P. G. Nutting, "A Study of Solutions of Silica and Alumina." *J. Wash. Acad.*, **32**, 117, April 15, 1942.

$pH = a \log C + b$ is evidently a correction to the initial energy which is $2.3RTb$ calories per mole.

A linear relation between pH and log concentration is therefore consistent with exact solution theory. In another paper a much more general relation between *any* two components of a solution will be discussed with observed data. Increased acidity on adding base to an acid solution and the reverse effect have also been shown to be expected by fundamental theory. The observed linear relation between ionic adsorption (or base exchange) and pH, multiple pH values, and the nature of glass electrode pH measurements require the further detailed consideration of adsorbed ions.

ELECTROLYTIC POTENTIAL.

The general theory of electrolytic solutions outlined above suffices for homogeneous solutions, those in which the ionic distribution is uniform with wall effects negligible. To deal with electrolytic potentials, solution theory must be extended to cover solutions containing nondiffusible ions, anions or cations more or less localized by membranes or adsorbing colloids or surfaces. The most general case to be considered is an adsorbed layer in which certain ions increase in mobility and decrease in concentration outward from a boundary according to definite laws.

After any solution has reached a steady state, since there is no net flow of either matter or energy in any direction in any portion of it, obviously as many molecules or ions must pass any unit plane in either direction as in the opposite. A simple application of either the kinetic or energy theory shows that for each species of particle (mass m constant) the concentration must vary inversely as the mobility defined as proportional to velocity squared since mu^2 is constant. When there is a concentration gradient, as in an adsorbed or osmotic layer, there must be an equal and opposite gradient of mobility or activity for each species. The value of the constant product (concentration times mobility) is obtained from RT and the molar concentration if desired. This reciprocity law fails only at solid walls when other forces come into play.

The law of electrical neutrality holds also for inhomogeneous solutions provided the volume considered is sufficiently large for the law of averages to apply. It must be applied with care when extraneous charges or valence forces are concerned. Likewise the law of mass action applies to all free ion pairs but must be modified to cover nondiffusible ions or ions partly immobilized. One of the simpler types of inhomogeneous solutions is that contained in a cell divided by a membrane freely permeable to the anions $A_1A_2 \cdots A_n$ and cations $B_1B_2 \cdots B_m$ but not to certain anions A_0 and/or cations B_0. The latter ions are nondiffusible only in the sense that they cannot pass the membrane.

Total anions = total cations on each side of the membrane, regardless of mobility. For monovalent ions completely dissociated, if the symbols represent molar concentrations, an application of the principle of virtual work shows that at equilibrium

$$\frac{B_1}{B_1^1} = \frac{B_2}{B_2^1} = \cdots \frac{B_m}{B_m^1} = \frac{A_1^1}{A_1} = \frac{A_2^1}{A_2} = \cdots \frac{A^1_n}{A_n} = 1 + \frac{A_0}{A} \text{ or } 1 + \frac{B}{B_0}, \tag{21}$$

the primes referring to ions in the compartment to which the non-diffusible ions A_0 (and/or B_0) are confined. A is the concentration of free anions that are competing with A_0, corrected for change in volume.

These remarkably simple ratios are still consistent with the laws of neutrality and of mass action and the ratios $H : H^1 = OH^1 : OH$ for water ions may be added to (21). Differences, if desired, may be obtained by subtracting unity from each fraction and multiplying out. Each ion pair has its own mass action constant despite the equality of the mass ratios. The Donnan equation $X^2 = Y^+(Y^- + Z)$ developed for a single pair of free ions is a limited special case of (21). According to (21), every species of cations loses the same amount of energy per mole in passing from a free to a restricted area, the same is true for the anions, an amount readily calculated since A_0 and A are known from the amounts put in.

After a Donnan equilibrium has been established between the solutions on either side of a semipermeable membrane, obviously neither solution will be affected if the membrane is replaced by an impermeable wall and the laws of homogeneous solutions discussed above will apply to each. They will differ in pH and osmotic pressure by amounts which may be measured or computed.

The next step toward a solution theory of adsorption is to consider a solution containing distributed colloidal micellae each capable of adsorbing certain species of anions or cations. In the "free" solution between these, all ions not adsorbed are free to move about as though no adsorbing particles were present. Electrical neutrality still holds so that both anions and cations must be equally adsorbed beyond the first layer, which may be held by an electric charge or by chemical valence. The Donnan relation between free and adsorbing areas still holds with but a single slight modification, a *change* of *phase* when ions are completely immobilized. This increases the energy of transfer between free and nondiffusing solutions. That there is a gradient of concentration outward from an adsorbing surface (such as $d \log B/dZ$) does not affect the overall energy difference since intermediate steps integrate out, leaving only the ratio (of ionic concentrations) of inner and outer layers.

Writing (21) for the simple case of water containing a single pair of ions of which the anion is adsorbed

$$\frac{H}{H^1} = \frac{A^1}{A} = 1 + \frac{A_0}{A} \quad \text{and therefore}$$

(22)

$$\frac{H - H^1}{H^1} = \frac{A^1 - A}{A} = \frac{A_0}{A}.$$

The increase in hydrogen ion concentration is therefore proportional to the concentration of adsorbed anions and (22) offers a simple theoretical explanation of the operation of the glass electrode pH meter. A charged glass electrode, adsorbing anions in proportion to their concentration, would give just the observed effects. Since the scale zero is arbitrary and spurious effects are compensated for, the scale reading at balance is an accurate measure of the adsorption. The dilution effect noted above ($pH = a \log c + b$) is to be expected in the range of complete dissociation with no side reactions. And of course adsorption proportional to pH is to be expected under similar conditions.

Multiple pH readings or buffer points are to be expected from (21) when a number of different species of anion are present, each with its own adsorption coefficient and none so outstanding as to overpower the rest. However, much detailed observation of special cases will be required to disentangle the laws governing their behavior.

Within the limits of a journal paper it is impossible to give more than a sketchy outline of a subject that would require a volume to present in detail and years of experimental work to clear up. However, some sort of coherent working theory, to be proved or disproved, has been needed as a guide in the fields of adsorption from solution and in pH measurements and this material is presented for what it may be worth in further work.

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

COLOR DESIGNATIONS FOR LIGHTS.

Since the development of the ISCC-NBS (Inter-Society Color Council-National Bureau of Standards) system of color names for describing the colors of drugs and medicines (*J. Research NBS*, **23**, 355 (September, 1939) RP1239), a need has been recognized for a system that would accomplish the same thing for lights. The case was made more urgent by the fact that conflicting names are often used in describing the colors of flares, landing lights and beacons, signal lights, and fluorescent and phosphorescent materials.

A tentative extension of the ISCC-NBS system was, therefore, worked out for lights and is described by Kenneth L. Kelly, research associate of the American Pharmaceutical Association, in the November number of the *Journal of Research* (RP1565). High-value hue names, for example red, pink, bluish purple are used, but not those of low-value, such as brown or olive. Color names including modifiers, as for instance pale, weak, or brilliant are not employed because the conditions of viewing are so variable that the problem is usually one of separating lights of different hues. The hue names are those used in the ISCC-NBS system and carry the same meaning.

The chromaticity ranges identified by each of these hue names are defined by areas on the ICI chromaticity diagram. The constant-hue boundaries center on the point representing standard illuminant C, and extend out to the spectrum locus. Comparisons are made between the dominant wave-lengths corresponding to the centers of the proposed hue-name ranges and similar values reported by a number of authorities. Comparisons are also made with the standard colors recognized in various specifications for marine, railway, aviation, and highway traffic signal glasses.

REACTIONS OF SILICA AND ALUMINA WITH LEAD OXIDE.

Lead oxide has been a constituent of ceramic glazes, glasses, and enamels since the inception of glaze and enamel decoration long before the Christian era. The reason for this is not difficult to deduce. PbO combines with difficultly fusible silica, which is the principal constituent of pottery, to form a glass at temperatures well within the range of the crude furnaces used by the ancients. The glass thus formed

* Communicated by the Director.

is sufficiently viscous to flow smoothly over the surface to be decorated or protected, and the characteristic high index of refraction gives it a pleasing brilliance. Although modern ceramic glasses are much more complex than the early lead silicates, lead oxide is still considered essential to the production of many vitreous enamels, pottery glazes, and artware as well as optical glasses.

About 10 years ago a comprehensive study of phase relations in binary and ternary systems of PbO combined with other oxides used in ceramics was undertaken at the Bureau by R. F. Geller and E. N. Bunting. Several papers have been published and the latest of these (RP1564 in the November *Journal of Research*) is a report on the partial systems PbO-Al_2O_3, and PbO-Al_2O_3-SiO_2.

The compositions investigated are limited practically to those containing over 50 per cent. of PbO. It is believed reasonably certain that PbO and Al_2O_3 combine to form the compound $PbO \cdot Al_2O_3$ and that a eutectic with PbO exists at about 865° C. and 94 per cent. of PbO. The compound appears to be unstable below the melting point, breaking down to give corundum and liquid.

In the ternary diagram, the greater portion is occupied by the stability fields of corundum and of mullite. The portion investigated disclosed the existence of at least 7 compounds. Of these, 3 are established ($8PbO \cdot Al_2O_3 \cdot 4SiO_2$, $4PbO \cdot Al_2O_3 \cdot 2SiO_2$, and $6PbO \cdot Al_2O_3 \cdot 6SiO_2$) and 4 are indicated by their optical and X-ray characteristics. The boundaries include 10 established quintuple points of which 6 are eutectics.

The report also contains a chart showing the indices of refraction of the various compositions as glasses, and gives the determined value of 2,040° C. for the melting point of Al_2O_3.

CHIPPING AND IMPACT RESISTANCE OF VITRIFIED CHINAWARE.

A manufacturer of vitrified chinaware recently requested information concerning the effect, if any, of variations in the hardness of chipping hammers on the apparent resistance of his product to chipping when tested in accordance with Federal Specification M-C-301a. The Bureau had been using the same hammer for years and had never investigated the effect of variations in the hardness of the steel, the Federal specification requiring only that the hammer be made of that material. A study was therefore undertaken using steel hammers of widely varying hardness. Advantage was taken of this opportunity to study also the effect of steel hardness on resistance to impact.

A total of 30 dozen 7-inch hotel-weight rolled-edge plates were subjected to chipping and to impact tests, using six tool steel chipping hammers and two impact hammers, representing a considerable range

in hardness which, expressed in terms of the Vicker's number, extended from 160 for the untempered steel to 720 for the hardest.

The results show that hammers varying in hardness from 470 to 655 are not damaged in the test and produce chipping values which do not differ significantly. To insure results that can be duplicated in different laboratories, the Federal specification should require a hammer hardened and tempered to a Vicker's number within this range.

Although the impact hammers had hardness numbers of 210 and 665, respectively, the results obtained with them were practically duplicates, and an impact hammer with a hardness in this range would be satisfactory.

Neither variations in water absorption nor in weight affected the chipping or the impact values of these plates, the absorption values for which ranged from 0.00 to 0.19 per cent.

The highest percentages of bottom chips were produced on plates having the least slope of the rim and consequently the least height from the base to the edge. Of 12 sections examined, those taken next to bottom chips also showed a materially greater horizontal distance from the point of impact on the edge through the body to the upper surface of the rim.

IRON AS A TANNING AGENT.

Our supply of vegetable tanning materials, as well as the chromium used to tan most of the garment and shoe upper leathers for both civilian and military purposes, depends largely upon ships and safe ocean transportation. The importance of developing domestic materials to meet any emergency is illustrated by the fact that only a short time ago the danger of a serious shortage of chromium was such that it was declared a critical material by the War Production Board. Since iron had been shown by previous investigators to offer some promise as a successful tanning agent and since an abundant domestic supply of this metal exists, an investigation of the use of iron salts for tanning with special attention to the replacement of chromium salts was undertaken by Joseph R. Kanagy and Ruth A. Kronstadt at the Bureau. At the present time the situation with respect to chromium for tanning has been greatly relieved by the utilization of low grade domestic ores in the manufacture of chromium salts. Nevertheless, the results of the Bureau's work are of interest.

These results, which are reported in RP1566 in the *Journal of Research* for November, indicate that ferric sulfate may be satisfactorily used if certain organic acids are added to the tanning solutions to stabilize them. Lactic, citric, gluconic, and hydroxyacetic acids were found suitable for stabilizing the iron tanning solutions at the pH

required for successful tanning. Without them the iron precipitates as the hydroxide, a form useless for this purpose.

Considerably more iron (Fe_2O_3) than chrome (Cr_2O_3) is required to tan a piece of leather. All hides tanned with the iron contained at least 10 per cent. of Fe_2O_3, whereas good leather can be prepared from chromium salts which contain only 5 per cent. of Cr_2O_3. Experiments with hide powder showed that as much as 25 per cent. of Fe_2O_3 combined under optimum conditions.

Iron tanning solutions appear to have properties similar to those of chrome tanning solutions. Results of accelerated aging tests on iron tanned goat and calf skins indicated that, on the average, the iron tanned leather is slightly less resistant to aging than the chrome tanned leather.

WATER-REPELLENT FABRICS.

The development of fabrics that shed water readily and yet permit the wearer to "breathe" through them is especially important to the armed forces. Such fabrics can give protection against all but very heavy rains, and since they only absorb water very slowly, they remain relatively light in weight even under adverse conditions. As a means of testing such water-repellent fabrics, an improved apparatus, referred to as a "drop-penetration apparatus," to simulate the action of rainfall, has been devised. Drops of controlled size fall at a constant rate upon the fabric to be tested. The length of time required for water to penetrate through the fabric is taken as a measure of its water-repellency, this time being indicated by means of an electrical signalling device. Water-repellent fabrics have been exposed to severe natural rainfall, as well as the action of the drop-penetration apparatus and good correlation has been found between the results obtained under the two conditions.

TESTS OF SYNTHETIC RUBBER.

The Bureau is coöperating with the Rubber Reserve Company in its efforts for the production of synthetic rubber of uniform, high quality. Careful control so as to secure uniformity is necessary, because the 11 synthetic rubber plants now in production are in widely separated localities from Connecticut to California and are necessarily operated by newly-trained and inexperienced personnel. Furthermore there are differences both in the processes and in the raw materials used. It is the desire of the Rubber Reserve Company, that the rubber from all plants shall be of such uniformity that it can be used interchangeably in the manufacture of rubber goods. To this end the Bureau is assisting in the development of well-defined specifications and in the improvement

and clarification of test methods. Samples from each plant are regularly tested at the Bureau and much cross-checking is done to keep the different laboratories in agreement. Standards which were "good enough" for natural rubber are not adequate for the testing of synthetic rubber.

TREADING AUTOMOBILE AND TRUCK TIRES.

The current shortage of rubber, necessitating maximum service from automobile and truck tires, has resulted in an increase in the practice of replacing worn rubber on the treads of used tires by processes known as treading, retreading, and recapping. When properly done, this practice has proved highly satisfactory, and results in greatly increased mileage at a very material saving in the amount of rubber used.

The Bureau has just issued a pamphlet, Commercial Standard CS108-43, that sets forth requirements that the industry considers representative of a high standard for treading automobile and truck tires. The standard covers inspection of the worn tire and the conditions necessary for satisfactory treading; quality of materials used; workmanship; and guarantee to the purchaser.

The establishment of the standard was requested by the National Institute of Treading Standards and the specification was adopted by a general conference held in Washington on September 16, 1942. The conference was attended by representatives of firms engaged in treading, firms that manufacture the equipment and the materials used, transportation organizations, tire rationing boards, and others interested in various phases of the subject. The specification adopted by that conference has been accepted by a large number of those interested, representing a major portion of the productive capacity of the industry.

The pamphlet, entitled "Treading Automobile and Truck Tires," includes such information as the membership of a standing committee for future revisions of the standard, a brief history of the project, and a list of firms, organizations, and individuals that have accepted the specification as their standard of practice. Copies may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price is 10 cents.

Phosphating Prior to Silver Plating of Steel.—(*Iron Age*, Vol. 152, No. 20.) The corrosion resistance of steel is usually not improved by the application of a thin coating of silver. On the other hand, phosphating the steel surface does improve the corrosive resistance. A combination of the two processes has been tried in the past but results have not been conclusive. A recent investigation of the subject, undertaken for the Electro-Chemical Society by Philip J. Le Presti, Rochester, has resulted in the finding that silver plating steel after phosphating markedly improves the adhesion of the silver to the steel. It appears that although most, if not all, of the phosphate coat disappears during the first stages of silver plating, the phosphate coat protects the steel surface during that brief interval before the silver is discharged and deposited.

The investigation indicated that with a zinc phosphate-phosphoric acid solution it is possible to deposit a phosphate coating on steel. If only a light phosphate coating (produced in about 1 min.) is used as a basis for silver plate, it is possible to obtain a smooth silver plate which shows a test for phosphate after stripping. If a heavy phosphate coat is applied, the silver strike will remove nearly all of the phosphate coating before striking is completed and expose a more highly etched steel surface, consequently a rougher silver surface will result.

Corrosion tests, comprising complete submersion in saturated NaCl solution, showed, after 4 hr. exposure, 50 per cent. more corrosion of the standard silver plate than of the phosphated silver samples. However, after 24 hr. exposure, the amount of rust seemed about the same for both standard and phosphated samples.

A light phosphate coat on steel before silver plating will protect the steel against oxidation. During silver deposition in the strike solution the phosphate coating will almost disappear, and the silver will deposit deep into the grain boundaries resulting in a firm anchorage of the silver deposit to the steel surface.

This interesting result suggests a simple solution of the ever present difficulty of preventing oxide or sulfide films on steel after careful cleaning preparatory to plating. The principle involved should be applicable to other metals beside steel; a thin protecting coating may be developed or applied to the clean metal surface during the last steps of the cleaning operation and be of such a nature and consistency that it will largely disappear during the first stages of the plating operation.

R. H. O.

THE FRANKLIN INSTITUTE

STATED MONTHLY MEETING, NOVEMBER 17, 1943.

At the stated monthly meeting of The Franklin Institute held in its Hall, a record attendance indicated much interest on the part of members in the work of the Institute and the Russian scientific film scheduled for this meeting.

The meeting was called to order at 8:20 P.M. by the Presiding Officer, Mr. Charles S. Redding, President.

After the playing of the National Anthem, the Chairman announced that the minutes of the last meeting had been printed in full in the November JOURNAL, and stated that unless there were corrections they would be approved as printed. They were so approved.

The Chairman then called upon Dr. Henry Butler Allen, Secretary.

Dr. Allen reported that since our last meeting the following increases in membership should be noted:

Sustaining	1
Active	66
Associate	29
Students	23
Total	119
Total membership as of November 17, 1943	5,570

He reported the loss the Institute has sustained in the death of George S. Cullen, who had joined the Institute in 1891 and had served as a valued and faithful member of the Committee of Science and Arts since 1900.

Dr. Allen then called the attention of the members to the Christmas Week Lectures for Young People, which will be held this year at 3 P.M. on Tuesday, Wednesday and Thursday, December 28, 29 and 30. He announced the lecturer will be Professor Richard M. Sutton, Department of Physics, Haverford College, who has chosen as his subject:

"Longer Arms . . . Sharper Eyes . . . Keener Ears
In war and in peace physics extends
man's senses."

The subject matter will be divided as follows:

On Tuesday: "The Long Arms of a Giant: Bombs and Balms of Aviation."
On Wednesday: "The Sharp Eyes of a Giant: Photography, Camouflage and Television."
On Thursday: "The Keen Ears of a Giant: Electronics, Radio and Radar."

Dr. Allen stated the price of the tickets will be $1.10 (including tax) for the series and suggested the desirability of a ticket to some young person as a Christmas gift.

The Chairman then introduced Dr. Ellice McDonald, Director of the Institute's Biochemical Research Foundation, who gave his annual report on the work of the laboratories. Inasmuch as practically all of the time of the Staff has been devoted to war work, very little could be said about what had been accomplished. Dr. McDonald stated, however, that the results had been eminently satisfactory. At the close of his remarks the Chairman expressed the appreciation of the audience for his report.

The second half of the meeting was devoted to a motion picture entitled: "Glimpses of Russian Science" which was shown at the Institute through the good offices of Mr. A. Portnoff of the American Russian Institute. The Franklin Institute was honored to have as a guest on this occasion Mr. Vladimir Bazykin, First Secretary of the Soviet Embassy, Washington, D. C., who was introduced by the Chairman to the large assemblage.

At the close of the film, Dr. Allen recalled the correspondence between Benjamin Franklin and Princess Dashkova, President, the Imperial Academy of Sciences at St. Petersburg, which stated that because of his outstanding scientific contributions Franklin was proposed and unanimously elected to honorary membership in the Academy.

Dr. Allen, commenting on the present meeting, said that it was not only an expression of good will between two great countries at the present time, but also represented a continuation on the part of The Franklin Institute of an alliance of real import from the past.

He suggested that a cablegram be sent to the Academy of Sciences of the U.S.S.R. to inform them of this meeting and to bring them expressions of good will and encouragement from a sister scientific institution. He said this action had the full approval of the Board of Managers.

Upon motion duly seconded and carried, Dr. Allen, as Secretary, was commissioned to send the following message:

"Prof. Vladimir Komarov
President, Academy of Sciences of the USSR
Moscow
Russia

American Traditions mark Benjamin Franklin, the Scientist, the Diplomat, the Ambassador of Good Will and Friendship among Nations.

The Franklin Institute of Philadelphia in coöperation with The American Russian Institute at a stated meeting held November 17, 1943, viewed with keen interest an unique Russian sound film showing glimpses of Soviet science, physical, chemical, physiological experiments of high attainments.

This month marks the one hundred and fifty-fourth anniversary of Benjamin Franklin's election to membership in the Russian Academy of Sciences.

The Franklin Institute takes this occasion, in the spirit of Benjamin Franklin, to send greetings to the scientists of the Soviet Union, with the belief that the interrelations of the Arts and Sciences between our two great countries will greatly further mutual understanding, good will and permanent peace."

This action was loudly acclaimed by the audience composed of members of the Institute and many Russian friends.

Adjournment took place at 10:10. Over four hundred people were present; with great reluctance, over two hundred had to be turned away.

November 17, 1943.

"MEET DR. FRANKLIN."

The Franklin Institute announces the publication, in book form, of thirteen important papers depicting the life of Benjamin Franklin. These articles were delivered in the Hall of The Franklin Institute four years ago and have since appeared in serial form in the JOURNAL of the Institute.

The lectures were delivered under the auspices of The Franklin Institute, the American Philosophical Society and the Pennsylvania Historical Society. The men invited to give them are well known throughout the country and have made the study of Franklin an avocation. Now for the first time available in book form, a limited number of copies will bring to the public such information as "Franklin the Scientist" by R. A. Millikan; "Dr. Franklin as the English Saw Him" by Conyers Read; "Self-Portraiture: The Autobiography" by Max Farrand;

"Franklin's Political Journalism in England" by Verner W. Crane; "Student of Life" by Robert E. Spiller; "Molding the Constitution" by George Wharton Pepper; "Philosophical Revolutionist" by Bernhard Knollenberg; "Looking Westward" by Gilbert Chinard; "The Printer at Work" by Lawrence C. Wroth; "Adventures in Agriculture" by Carl R. Woodward; "Friend of the Indians" by Julian P. Boyd.

The opening and concluding talks on Franklin, which also appear in the book, were given by Carl Van Doren, winner of the Pulitzer Prize for his admirable work on Franklin, published in 1939.

Further information may be procured by writing to the Office of the Editor, Journal of The Franklin Institute, Benjamin Franklin Parkway at Twentieth, Philadelphia 3, Pa.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, November 10, 1943.)

HALL OF THE COMMITTEE,
PHILADELPHIA, NOVEMBER 10, 1943.

DR. JOSEPH S. HEPBURN *in the Chair.*

The following report was presented for final action:

No. 3126: Newcomen Medal.

This report recommended the award of The Newcomen Medal to Harold Gardiner Bowen, of Washington, D. C., "In consideration of his long record of service with a group of engineers, whose work is now such a vital part of the life of our nation, and particularly in view of his outstanding advocacy of the advance in steam engineering in this branch of our national defense, as represented by the increase in steam pressures and temperatures used on equipment installed on its ships."

JOHN FRAZER,
Secretary to Committee.

MINUTE ADOPTED BY THE COMMITTEE ON SCIENCE AND THE ARTS ON THE OCCASION OF THE DEATH OF MR. WARREN POWELL VALENTINE.

The Committee on Science and the Arts records with deep regret the death of its very able and devoted member, Warren P. Valentine, on October 6, 1943, at his home, 622 Longacre Boulevard, Yeadon, Pennsylvania. A member of the Institute since 1927, Mr. Valentine became a member of this Committee in 1929. For fourteen years he served on numerous Sub-Committees and always displayed a very high standard of work. He always insisted that any report to the Science and Arts Committee should be prepared with the utmost care and accuracy.

Mr. Valentine was born in Terre Haute, Indiana, October 12, 1875, one of the six sons of Harriet M. and William Valentine. During the early years of his life, spent in Indiana and Tennessee, he developed an interest in mechanics, and, with a brother, built one of the first automobiles in Richmond, Indiana. As a young man, largely self-educated, he moved east where he engaged in sales work. Later, he became an instructor in the Trades Apprentice School of the Westinghouse Electric and Manufacturing Company in East Pittsburgh, Pennsylvania, after which he was associated with Dean Pump Company, of Holyoke, Massachusetts, in an engineering capacity. During the past twenty-eight years, he was District Manager in Philadelphia for the National Transit Pump and Machine Company doing engineering work, which included, mainly, the design and patenting of pumping equipment.

Being deeply interested in, among many other things, optical scientific instruments, he received in 1928 the Edward Longstreth Medal of The Franklin Institute "In consideration of the meritorious work shown in the improvement of the mechanical and optical parts of the Abbé Refractometer, thereby increasing its accuracy."

Mr. Valentine was married in 1903 to Miss Florence Eleanor Birdsall, who, with a son, two daughters, and three grandchildren, survives him.

Enjoying the respect and confidence of his colleagues, he rendered excellent service to the Committee on Science and the Arts throughout the period of his membership, and his fellow members deeply regret his passing.

BE IT RESOLVED, That this Minute be spread upon the records of the Committee on Science and the Arts and a copy of it sent to Mrs. Valentine.

November 10, 1943.

LIBRARY NOTES.

The Committee on Library desires to add to the collections any technical works that members would wish to contribute. Contributions will be gratefully acknowledged and placed in the library. Duplicates received will be transferred to other libraries as gifts of the donor.

Photostat prints of any material in the collections can be supplied on request. The average cost for a print 9 × 14 inches is thirty-five cents.

The library and reading room are open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays from two until ten o'clock P.M.

RECENT ADDITIONS.

AERONAUTICS.

CLANCEY, VERNON J. Chemistry and the Aeroplane. 1943.

ASTRONOMY.

NEELY, HENRY M. The Star Finder. 1943.

CHEMISTRY AND CHEMICAL TECHNOLOGY.

CREIGHTON, H. JERMAIN. Principles and Applications of Electrochemistry. Volume 1: Principles. Fourth Edition. 1943.

Electrochemical Society. Transactions 1942. Volume 82. 1943.

OLSEN, ALLEN L., AND JOHN W. GREENE. Laboratory Manual of Explosive Chemistry. 1943.

OTT, EMIL, Editor. Cellulose and Cellulose Derivatives. 1943.

PIGOTT, E. C. The Chemical Analysis of Ferrous Alloys and Foundry Materials. 1942.

REMICK, A. EDWARD. Electronic Interpretation of Organic Chemistry. 1943.

SCHMIDT, CARL L. A. Addendum to The Chemistry of the Amino Acids and Proteins. 1943.

THORPE, JOCELYN FIELD, AND M. A. WHITELEY. Thorpe's Dictionary of Applied Chemistry. Fourth Edition. Vol. 6. 1943.

ELECTRICITY AND ELECTRIC ENGINEERING.

PREISMAN, ALBERT. Graphical Constructions for Vacuum Tube Circuits. First Edition. 1943.

REYNER, J. H. Cathode-Ray Oscillographs. Second Edition. 1943.

STARR, A. T. Electric Circuits and Wave Filters. Second Edition. 1943.

ENGINEERING.

SPIELVOGEL, S. W. Piping Stress Calculations Simplified. First Edition. 1943.

HYDRAULIC ENGINEERING.

BARROWS, H. K Water Power Engineering Third Edition. 1943.

HYGIENE.

LEHMANN, K. B., AND F. FLURY, Editors. Toxicology and Hygiene of Industrial Solvents. 1943.

MATHEMATICS.

EISENHART, LUTHER PFAHLER. An Introduction to Differential Geometry. 1940.

MECHANICAL ENGINEERING.

KRISTAL, FRANK A., AND F. A. ANNETT. Pumps. First Edition. 1940.

MINING AND METALLURGY.

American Institute of Mining and Metallurgical Engineers. Transactions. Institute of Metals Division. 1943.
COONAN, FREDERICK L. Principles of Physical Metallurgy. 1943.
CROOK, WELTON JOSEPH. Metallurgical Spectrum Analysis with Visual Atlas. 1935.
GIVEN, IVAN A. Mechanical Loading of Coal Underground. First Edition. 1943.
MONDOLFO, LUCIO F. Metallography of Aluminum Alloys. 1943.
ZMESKAL, OTTO. Radiographic Inspection of Metals. 1943.

METEOROLOGY.

TREWARTHA, GLENN T. An Introduction to Weather and Climate. Second Edition. 1943.

MILITARY SCIENCE.

SMITH, WINSTON O. The Sharps Rifle. 1943.

PHYSICS.

BINDER, R. C. Fluid Mechanics. 1943.
JACOBS, DONALD H. Fundamentals of Optical Engineering. First Edition. 1943.
LUHR, OVERTON. Physics Tells Why. 1943.
ZEMANSKY, MARK W. Heat and Thermodynamics. Second Edition. 1943.

SCIENTIFIC ESSAYS.

SHAPLEY, HARLOW, SAMUEL RAPPORT, AND HELEN WRIGHT, Editors. A Treasury of Science. 1943.

STEAM ENGINEERING.

KEARTON, WILLIAM J. Steam Turbine Operation. Fourth Edition. 1943.

SURGERY.

SHAAR, C. M., AND FRANK P. KREUZ. Manual of Fractures. 1943.

NOTES FROM THE BIOCHEMICAL RESEARCH FOUNDATION.

The Preparation and Properties of a New Type of Typhoid Vaccine: A Preliminary Report.—RICHARD W. LINTON, ROBERT K. JENNINGS AND KATHRYN V. HUFFMAN. As a result of work begun in February, 1943, we are now able to report, in a preliminary form, the successful development of a typhoid vaccine which we believe to be superior to the present commercial product in immunogenic capacity for mice. Our vaccine is practically free from non-specific antigens derived from the medium, and its production requires little manipulation of the organisms.

It is the present practice to prepare typhoid vaccines by growing the organisms on an agar substrate rich in soluble protein material. The bacilli are washed from broad surfaces of this medium and suspended in physiological saline. They are then killed and diluted to the desired concentration.

Our vaccine consists of a direct preparation made by growing the organisms in a liquid medium so simple in composition that it may be used for injection. In spite of the simplicity of the medium, however, excellent cultures are obtained.

The medium used contains 0.5 per cent. sodium phosphate (dibasic), 0.01 per cent. magnesium sulfate and 1.5 per cent. of a casein-digest solution. The latter is a preparation obtained by the tryptic digestion of a 10 per cent. suspension of casein. It is completely dialyzable and contains 9 to 12 mg. of nitrogen per ml.

One cubic milliliter of medium thus contains about 0.005 g. of Na_2HPO_4, 0.0001 g. of $MgSO_4$ and about 0.15 mg. of organic nitrogen. Since the culture is so heavy that usually it must be diluted about five times for use as a vaccine, the components of the vaccine not attributable to the organisms themselves become correspondingly smaller.

None of the antigenic constituents is lost, since it is not necessary to wash the bacteria. Whether due to this fact or because growth in liquid media approximates more closely the natural habitat of the organisms, the vaccine has proved more efficient than the commercial product in protecting mice against experimental infections with typhoid organisms. In a typical experiment, seven mice out of a group of 27 immunized by our direct vaccine died when inoculated with the test dose of approximately 100,000 virulent organisms, while 13 out of a group of 28 mice which had been treated first with commercial vaccine died with the same dose of living organisms.

The explanation of the excellent growth on such a simple medium lies in the use of aeration in conjunction with preliminary administration

of CO_2 gas. Carbon dioxide is passed through the medium for two minutes at the time of inoculation, followed by a stream of compressed air which is allowed to bubble through the culture for the remainder of the growth period, which is generally between 18 and 24 hours. The crop of cells obtained is about five times as heavy as when the cultures are not aerated.

Twelve liters of culture which have been aerated until maximum growth has been attained can be readily rendered sterile by the addition of 0.5 g. of phenylmercuric acetate dissolved in a little water by the aid of heat. Subcultures taken at an interval even as short as five minutes after the addition of the disinfectant showed no growth upon incubation. Since this concentration of the phenyl compound may safely be injected, we have used it routinely to kill the organisms.

Summary: A preliminary report is made of the production and immunological properties of a typhoid vaccine made directly from a culture of typhoid in liquid medium. Such a culture permits the full use of all the antigenic material elaborated by the organisms and results in a degree of immunization in mice superior to that given by the usual agar-grown vaccine. The uninoculated medium itself is so simple that it contains almost no material which might prove antigenic. Growth is promoted by the use of aeration after an initial treatment of the culture with carbon dioxide. The final culture is killed by dilute phenylmercuric acetate. It is regularly so heavy as to require dilution before use as a vaccine and no other manipulation is required.

BOOK REVIEWS.

TUNGSTEN—ITS HISTORY, GEOLOGY, ORE-DRESSING, METALLURGY, CHEMISTRY, ANALYSIS, APPLICATION, AND ECONOMICS, by K. C. Li and Chung Yu Wang. 325 pages, illustrations, 16 × 23 cms. New York, Reinhold Publishing Corporation, 1943. Price $7.00.

Much interest is attached to this strategic metal by world powers. Inasmuch as tungsten enters principally into the manufacture of tool steels it was much sought for in the years immediately preceding the war by the axis countries. Also, because of its principal use, it has considerable peace-time demand everywhere and there are good prospects for increasing this demand. For instance, the use of tungsten steel for high-temperature work such as gas turbines and generators is new and is not yet widely known.

This book meets a need in giving a well-rounded story of tungsten. It begins with a history of tungsten which is rather brief, since the industrialization of the metal began only in 1847, and the public's attention was first drawn to it at the Paris Exposition of 1900. Considerable space is devoted to the geology of tungsten. Here are discussed the genesis of the ore, associated minerals and their paragenesis, and then a study is made of the tungsten deposits of the world by countries and sections of countries. Ore-dressing of tungsten is the next subject, where methods generally adopted for concentration and improvement of concentrates are taken up. These include gravity, flotation, magnetic, electrostatic, pneumatic, float and sink, and roasting and bleaching. It is shown that the amenability to treatment of the ores or of their concentrates with respect to any of the methods or a combination of the methods depends upon the types of ores or concentrates and their associated minerals.

Under the heading of the metallurgy of tungsten the various methods and processes that have been proposed or adopted for the treatment of tungsten ores are discussed under classifications of (1) Decomposition of Tungsten Ore, (2) Purification of the Ore, and (3) Production of Tungsten Powder. In large measure patents are the source material of this discussion. The next subjects are the chemistry of tungsten and the analysis of tungsten. The latter includes procedures for determination in ores. The latter part of the book is devoted to industrial applications and the economics of tungsten. The former is divided into ferrous alloys (after Bullens), non-ferrous alloys, tungsten carbides, electrical equipment, tungsten compounds and miscellaneous applications. The latter, economics of tungsten, does not include the present period 1938 to date, on account of the present world turmoil. Appendixes contain data on the terms for the purchase of tungsten ores.

The work is well prepared from a multitude of sources. It is presented in an admirable fashion. Anyone interested in any way in tungsten should benefit by its broad coverage.

R. H. OPPERMANN.

SEMIMICRO QUALITATIVE ANALYSIS. A Course in Applied Chemical Equilibrium by John F. Flagg. 140 pages, tables and diagrams, 15 × 23 cms. New York, D. Van Nostrand Company, Inc., 1943. Price $1.50.

The field of semimicro qualitative analysis has attained its present position from a combination of old and new techniques dating from the early part of the century. That it has a definite place in a practical sense is unquestioned. It is a branch of qualitative analysis which is valuable from the teaching standpoint by giving a working knowledge of the theory and practice of inorganic chemistry. It has other angles of value too, viz., its practicability in industry and medicine, as well as its place in a program of liberal education where it teaches patience, self-reliance, orderliness, etc.

The textbook at hand has been built up from procedures for a one-semester course at the University of Rochester. Based on the chemical equilibrium idea it presupposes a knowledge of general chemistry including such fundamentals as atomic structure, valence colloids etc.

There are three parts to the book. In the first, after a general introduction, the law of chemical equilibrium is developed and then it is shown how this may be applied to numerous cases of, first, homogeneous equilibrium, then heterogeneous processes. Following this there is a discussion of oxidation-reduction reactions. These certain special techniques and operations are described which refer especially to the semimicro analysis over the ordinary qualitative analysis in any form. These include common operations as precipitation, separation and washing of precipitates and mixing reagents. Brief reference is made to semimicro apparatus and directions with regard to the laboratory notebook and the schedule of laboratory work.

Part two of the book consists of a list of and detailed procedures for experiments in a course devoting approximately six hours per week to laboratory work. First cation analysis is taken up, then the analysis of the anion constituents. For advanced work the procedures for the analysis of ferro alloys are given. These acquaint the student with the chemistry of less familiar elements and provide working directions for the analysis of this important and specialized class of alloys. The third and last part of the book is an appendix which contains tabular and other information, rounding out completeness of the work.

The material is well presented, including illustrative problems. The book can very well fit into a course of school instruction. It is also of value to those practicing qualitative analysis.

R. H. OPPERMANN.

PROPAGATION ELLIPSOÏDALE, RELATIVITÉ, QUANTA, by H. Varcollier. 398 pages, 16 × 25 cms. Alger, Baconnier Frères, 1942. Price $4.00.

To those who feared that there would be no more contributions to French research until the soil of France once more was free, it is most heartening to learn that in North Africa works on pure, abstract science are even now appearing. The publishing firm of Baconnier Frères in Algiers, carrying on under conditions of appalling difficulty, are helping to maintain in their city a French intellectual center and earning the gratitude of us all.

Their present volume by M. Varcollier is an account of experiments based on the theory of the ellipsoidal propagation of light. Whether or not this theory may win final acceptance is for the future to show, but it has attracted the attention of many physicists, especially as an explanation of the Michelson experiment.

At present the great problem in physics is to establish a unity between the theories of relativity and of quanta, and M. Varcollier's thesis is that an ellipsoidal reconstruction of the two theories would supply this unity. After explaining by this hypothesis the famous relativity experiments, he discusses its application to the quantum theory, and tries to show that it may well become the means of providing the logical connection between the principle of continuity and the mysterious fact that radiant energy is emitted and absorbed by quanta.

North Africa, that home of ancient learning, has been hospitable to the culture of France. Perhaps, when the day of liberation arrives, it may be from Algiers that French science will be inspired not only to take its former place but to press forward to a future even more glorious.

E. E.

METALS AND ALLOYS DATA BOOK, by Samuel L. Hoyt. 334 pages, tables, 18 × 26 cms. New York, Reinhold Publishing Corp., 1943. Price $4.75.

This is an unusual book covering an unusual subject. Not classifying as a handbook nor as a text, about the best description that can be given is what the author has named it —a data book. He states that it is the outgrowth of an attempt to accumulate reliable data on metals, and he found that by leaving out descriptive and explanatory matter, and including only data, he could well cover this large field of metals and alloys.

The data are arranged under the following headings—hardness tests, the wrought steels, the cast steels, stainless steels, the cast irons, heat- and corrosion-resistant casting alloys, the non-ferrous alloys, additional metals, and general data. Needless to say, the information is great in extent and in many cases of a nature not readily available. Both the viewpoints of the metallurgist and the engineer are considered, not only in the kind of data, but in the method of its presentation too. That many sources of the data were used is evident, and the

author states that much of it he has been able to check against more than one reliable source or to select from sources that are held to be reliable. Special mention should be made about the importance of the data on the heat-treating steels and the effect of cold work or work-hardening, both of which are quite up-to-date in method and content.

When examining a data book of this nature, the question arises "Can any desired information be found quickly?" It is probably safe to say that one must become familiar with the arrangement of any data book before it becomes a good useful tool. The present book is no exception, but the author has taken great pains to overcome this handicap by his masterly arrangement, the very good table of contents in the front, and the comprehensive subject index in the back. Those interested in metals and alloys will do well to examine this book.

R. H. OPPERMANN.

DRYING AND DEHYDRATION OF FOODS, by Harry W. Von Loesecke. 302 pages, illustrations, 16 × 23 cms. New York, Reinhold Publishing Corp., 1943. Price $4.25.

While the dehydration of foods is not by any means a new industry, it did receive a tremendous impetus in World War I. After that war only the production of dried onions, garlic, parsley and chili survived and now with World War II the dehydration industry has taken on a new life. Today, the industry is greater than it has been at any time in its history and it is expanding rapidly. After this war ends, it is not likely that this industry will collapse so completely as it did after the First World War. There will be greater need for its continuance and much more will be known about it. Those interested in food dehydration, therefore, will welcome an up-to-date treatment.

This book is a compilation of the latest practical information dealing with this subject. It consists of ten chapters on the following topics—types of dehydrates, sun-drying and dehydration of fruits, dehydration of vegetables, dehydration of eggs, of milk, of butter, of meat, of fish, and beef blood, plant sanitation, costs of dehydration, nutritive value of dried and dehydrated foods, packaging and storage, methods of analysis and reconstruction of dehydrated foods. Within the limits of these chapter headings, the data covered are well presented and of practical value. The treatment is not exhaustive nor is there given a complete picture of the science of food dehydration. There is much research and development that is not covered here; in fact were the book to cover this phase of the subject, it would not be long before new material would make the book obsolete.

The many references from which the book was written are listed, and at the end there is a considerable patent list. The book is well written. A first hand knowledge by the author is very apparent. It provides much workable, valuable information.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

Tungsten, by K. C. Li, M.E., A.R.S.M., and Chung Yu Wang, M. Inst. M.M. 325 pages, charts and illustrations, 15 × 24 cms. New York, Reinhold Publishing Corp., 1943. Price $7.00.

The American Annual of Photography, Volume Fifty-Eight, 1944. 206 pages, illustrations, 18 × 25 cms. Boston, American Photographic Publishing Company, 1943. Price $1.50, paper.

A Short Course in Quantitative Analysis, by Hobart H. Willard, Ph.D., N. Howell Furman, Ph.D., and John F. Flagg, Ph.D. 253 pages, tables and diagrams, 14 × 22 cms. New York, D. Van Nostrand Company, Inc., 1943. Price $2.50.

The Science of Explosives, An Introduction to Their Chemistry, Production, and Analysis, by Martin Meyer. 452 pages, illustrations, 15 × 22 cms. Thomas Y. Crowell Co., New York, 1943. Price $4.50.

Elastic and Creep Properties of Filamentous Materials and Other High Polymers, by Herbert Leaderman, Sc.D. 278 pages, illustrations, 18 × 26 cms. Washington, D. C., The Textile Foundation. 1943. Price $2.00.

CURRENT TOPICS.

ARMY AND NAVY NOTES.

The Sperry Automatic Sight.—(*Army Ordnance*, Vol. XXV, No. 140.) The Sperry automatic computing sight has helped make the B-17 Flying Fortress bomber the deadliest heavy-weight fighter of the war. The sight, with an integral part of the Sperry designed upper local and lower ball turrets, makes the caliber .50 machine guns effective at ranges up to 1,000 yards. Compared with the accurate ranges of enemy pursuit airplanes, this gives U. S. gunners a decided advantage that enables them to destroy Axis attackers before they can get close enough to deal telling blows.

The computing sight automatically figures the "fall" of the bullet because of gravity, the ballistic deflection caused by wind, and the amount of "lead" required to hit a target. Duck hunters realize that to hit a moving bird, the gunner cannot sight directly on the target. If he does, the bird will be out of the line of fire by the time the shot reaches its intended objective.

Shooting from a fast moving bomber at a faster moving target makes the problem more involved. Even though the muzzle velocity of caliber .50 shells is 2,700 feet a second, the correct computation of lead, fall, and deflection is the essential ingredient of successful aërial gunnery.

As far as the gunner is concerned, when using the automatic device, he seems to aim directly at the target. The sight, however, points the guns automatically and continuously at the spot where the target will be when the bullets arrive. The gunner makes no mental calculations. Trained to recognize the various types of enemy pursuit planes, he has only to adjust the sight control to correspond to the dimensions of the attacker. If, for instance, the attacker has a wing spread of forty feet, the operator twists the knobs to "40" on the dial, much like tuning a home radio.

Peering through the reflecting glass atop the sight, he must get two illuminated vertical lines on the target—a line at the outermost tip of each wing. This he does by controlling the movement of the turret and by operating a foot treadle which spreads the verticals to keep them on the wing tips as the pursuit plane, moving at terrific speed, roars closer, thus automatically and continuously setting the proper range.

R. H. O.

Welded Bayonet Clips Replace Forgings.—(*Iron Age*, Vol. 152, No. 11.) By eliminating extensive machining operations which are necessary in many fabricating methods, arc welding has become a valuable time saver in the production of hundreds of products essential to the war effort. A notable example of the economies thus effected is indicated in the welding of bayonet clips at Pratt Industries, Inc., Frankfort, N. Y.

The original clip was machined from a forging—a slow and expensive operation. The Ordnance Department suggested that the clips be produced from seamless tubing, forming the part in the dies, but this was given up as too

difficult a procedure. After calling in representatives of the Lincoln Electric Co. for a recommendation, it was decided that the clips could best be made by changing to a welded design, placing the welds at the top of the band. This choice was dictated primarily by requirements of forming the part.

The present method of manufacture is to make these stud bands from flat blanks of SAE 1020, measuring $1\frac{1}{2} \times 4.350 \times 0.072$ in. gage. This blank then goes through three punch press operations and then comes to the welding fixture. Twelve or more of these individual bayonet stud bands are placed on a mandrel in the welding fixture and the air-operated jaws bring these up against a copper fin which holds the dimension across the neck and at the same time permits 100 per cent. weld penetration. This group of parts is then welded without breaking the electric arc and emerges as a long piece of tubing which is then broken apart into the individual bayonet stud bands.

Despite the close tolerance of plus or minus 0.005 in. across the face and plus or minus 0.0025 in. across the neck, very few rejects are encountered and it has been possible greatly to reduce the machining time.

This procedure has proved very rapid and very satisfactory, as two men with one welding machine can produce several hundred stud bands per hour. The helper loads and unloads the mandrels and breaks the bands apart into individual units as they come from the welding operation.

R. H. O.

New Powerful Fuel Can Now be Made.—(*The Oil Weekly*, Vol. III, No. 1.) Described as the most powerful hydrocarbon known for use in internal combustion engines, triptane is a product promising to enhance greatly the performance of present day aircraft engines and to make possible the design of future engines of even greater power and efficiency, when used as a component of aviation gasoline.

The importance of triptane has been greatly increased through a discovery which makes possible immediate commercial production with materials which are adequately available. Heretofore, triptane has been a laboratory curiosity, made by an impractical and highly expensive method, which required consumption of critical materials. Therefore, it could not be supplied to the fighting forces.

Dr. Vladimir Haensel, research chemist, and Prof. V. N. Ipatieff, director of chemical research of Universal Oil Products Company, together with Universal's technical staff, have developed a method which makes possible the production of triptane for less than $1 a gallon. The discovery is expected to give the United Nations the most powerful fuels with which to fly.

The process yields not only triptane but also two other valuable hydrocarbons desirable in aviation blends.

The raw materials are condensable gases produced in petroleum refineries as by-products of catalytic and non-catalytic cracking or reforming of petroleum oils. The catalysts are readily available in large quantities. No special equipment or materials used in the process plant are necessary other than regular equipment employed in refineries. Temperatures and pressures employed are within refinery experience.

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